simtec®
SILICONE PARTS

LSR and
LSR 2-Shot
Innovative Technology

Table of Contents

Introduction

Liquid Silicone Rubber (LSR) is everywhere… your car, your home, the hospital… anywhere the material properties of LSR can bring benefits. With its incredibly versatile characteristics, such as thermal resistance, low compression set, thermal conductivity, chemical inertness, water repellency, and biocompatibility (and more), the potential number of applications for which LSR is the ideal material is limitless, and we are only beginning to explore the possibilities.

Since LSR is comprised of Silicon, the second most common element in the earth's crust, LSR is not only versatile in its uses, but it is also derived from a highly sustainable resource. This material is the present and the future.

At SIMTEC, we are exclusively focused on the fully automated, customized production of LSR parts, LSR over-molded parts, and LSR 2-Shot (LSR/Thermoplastic) injection molded components. It is this focus that has allowed us become one of the leading US based LSR injection molding companies, and as such, we hope to be able to share our knowledge and experience with companies that are looking for Liquid Silicone Rubber Solutions.

LSR and LSR 2-Shot Innovative Technology is a compilation of articles and technical papers that further define the material, its benefits, applications, and how it is processed. We hope you find this information to be both informative and helpful as you familiarize yourself with this highly adaptable material.

Thank you for downloading and enjoy!

SIMTEC Silicone Parts, LLC

Enrique Camacho

President

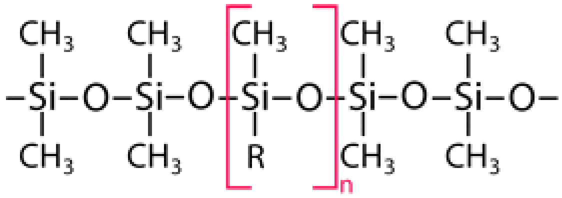
Chapter 1

Material and Properties

Material and Properties

A Versatile Material

Liquid Silicone Rubbers (LSRs) are molecules formed from a basic silicone oxide backbone.



Though some characteristics will remain the same for all LSRs, by varying certain side groups [R] (in this case CH3) of the structure, the material may be tailored to meet specific functions or requirements. Therefore, there can be many different LSR materials, each with different characteristics. LSRs have an extreme temperature range performance. At their pure state they will be stable from -50˚C to 180˚C. With the addition of stabilizers, the material can remain stable up to temperatures over 250˚C, and with the use of special compounds a low temperature flexibility of -90˚C can be achieved. LSRs are naturally transparent but may be easily colored by use of non-hazardous pigments. They have excellent chemical and oil resistance, are very stable, and are highly resistant to oxidation, light, UV, and X-rays.

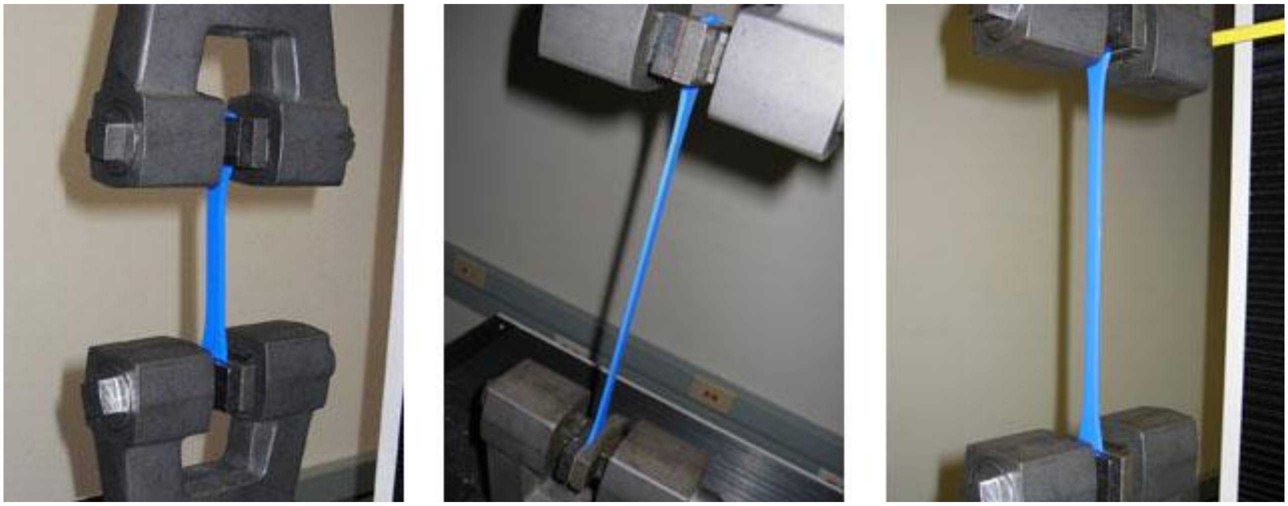
Liquid silicone rubbers do not contain any plasticizers, stabilizers, or promoters. Their exceptional flex characteristics are due to their unique chemistry. As a cross-linked material, LSR will withstand extreme temperatures with no heat aging and will maintain its mechanical properties and resilience over time. The material is cured through a process that contains non-hazardous substances; therefore, even in an under cured part, there is no threat of hazardous chemicals being released.

There are many different LSR grades available. Some examples include: electrically conductive, medical grade, FDA compliant, self-adhesive, self-lubricating, and various combinations of these.

Electrically conductive grades are usually carbon filled to the desired conductivity. Medical grade materials are prepared under rigorous testing and regulations to assure superior quality and adherence to safety standards. There are many different kinds of self-adhesive LSRs. In general, LSRs have outstanding compatibility with thermoplastics, but many formulations are available so as to fit many different applications. The most general formulations provide direct strong bonds onto most thermoplastic surfaces and metals including aluminum, magnesium, and steel. When over-molding to thermoplastics with high curing temperatures, glass-filled temperature resistant thermoplastics such as Polymides, PBTs, and PCs are preferred.

Superior Properties

In a variety of markets, properties of liquid silicone rubbers make them stand out over any other materials. LSRs are translucent, odorless, and tasteless. They are considered hypoallergenic and a material that will prevent bacteria or mold growth due to their inorganic molecular backbone. Silicone rubbers stand out with their outstanding mechanical properties. Their excellent heat range and weather resistance, combined with their low aging, make LSR parts exceptionally resistant; they will not become brittle over time.



Figures 1-3: Demonstration of superior elongation and tear resistance

Silicone rubbers are highly resilient materials. Cured during processing to create a strong intermolecular cross-linked structure, this structure will provide extreme elongation of the material with no permanent deformation and a higher tear resistance.

LSR is a high resilience material both in elongation and compression. When the material is compressed it will create an equal opposing force that will not change over time, making it great for seals and gaskets. LSR materials are cross-linked, which will prevent any creep or stress relaxation problems.

Variable Properties for Diverse Applications

Typical ranges for properties have been provided on the following table as a reference. Ranges shown are approximate and depend on the individual materials. However, these values are the most commonly seen in the market today:

Specific Gravity	Durometer (Shore A)	Tensile Strength (psi)	Tear Strength (ppi)	Elongation (%)
1.07-1.14	5-70	400-1520	50-590	150-980

SIMTEC's Core Processing Expertise

Our advanced molding technology, high precision molds, and cold runner systems lead to flash-free parts. Our expertise in the technology and materials allows us to optimize the process leading to lowest possible cycle times and best product quality.

When comparing our LSR injection molding process with other processes for making rubbers, LSR high-precision injection molding stands out in volume, purity, and quality. LSR purity stands out over any thermoplastic elastomer, polyurethane, or natural rubber. There is no ash content on cured parts, and parts may be made completely and perfectly transparent. Unlike with peroxide-based vulcanizations, there is perfect batch-to-batch consistency. This is made possible because of the simplicity of the materials to be mixed and the use of advanced automated mixing systems. High-cavitation molds provide a high volume of parts in shorter periods of time. These factors together lead to shorter cycle times, reliable consistency, and superior—and lasting—product quality.

Chapter 2

Viscoelastic Behavior of LSR

Silicone Elastomers 2011; December 6-7, 2011 – Chicago, IL USA

Viscoelastic Behavior of Liquid Silicone Rubber

Tim A. Osswald[1,2], Juan Pablo Hernández[2], Miguel Hidalgo[2], Natalie Rudolph1[1,2] and Katerina Sánchez[2]

SIMTEC Silicone Parts, LLC
Miramar, FL 33025
Website: www.simtec-silicone.com; Email: info@simtec-silicone.com

ABSTRACT

Polymers are both solid and liquid at the same time, regardless of the temperature. However, during processing and usage they appear to be either in the liquid or solid state. This is due to the density and the mobility of the molecule chains of the polymer. Silicone rubber has particularly good properties for applications that require both absorption as well as transmission of vibrations. This paper presents the fundamental behavior of liquid silicone rubber, addressing the time-temperature dependence of storage and loss moduli, as well as their development during cure. The whole range between viscous and perfectly elastic behavior, and their interaction is demonstrated with measurements and simple models.

INTRODUCTION

Over the past 60 years, silicone rubbers have become increasingly popular in industry, mainly because this material maintains its mechanical and electrical properties over a wide range of temperatures. It is the natural choice in many applications ranging from aerospace and automotive to medical and high technology devices [1 – 4]. It is commonly used for the production of seals in the automotive and aerospace industry, connectors and cables for appliances and telecommunications, implants and devices for medical purposes, and packaging and baking pans for the food industry. Silicone rubber is a family of thermoset elastomers that have a backbone of alternating silicone and oxygen atoms with methyl or vinyl side groups. As with thermosets and elastomers, the vulcanization process of silicone rubber, is dominated by an exothermic and irreversible chemical reaction called cure, where a three dimensional network is formed, in which each chain is connected to all others by a sequence of junction points and other chains. Since cross-linked silicone rubber has a relatively low crosslink density a silicone rubber product is flexible and elastic, with excellent viscoelastic behavior that is set during cure. The curing process improves the general properties of the final product and provides resistance to heat, due to the fact that these network polymers do not melt upon heating [5 – 8]. Two types of reactions lead to cross-linked silicone rubber depending of the catalyst used for the curing reaction: peroxide and platinum [9 – 12].

Silicone rubbers can be classified according to the polymer employed and the curing process as low-temperature-curing rubbers (RTV – Room Temperature Vulcanization) and high-temperature-curing rubbers (HTV – High Temperature Vulcanization). RTV silicone rubbers come as a soft paste or a viscous liquid. HTV silicone rubbers come in two different physical states: liquid and solid and are therefore called Liquid Silicone Rubbers (LSR) and High Cure Rubbers (HCR) or solid silicone rubbers. Because they exhibit a high viscosity solid silicone rubbers, commonly referred to as high consistency silicon rubbers, are processed in the same way as common organic rubbers [13].

Solid silicone rubbers (HCR) are formed using linear polymers with molecular weights between 400,000 – 600,000 g/mol. These polymers contain an average of 6,000 siloxy units and are water clear Newtonian liquids with viscosities between15,000 – 30,000 Pa-s. Solid silicone rubbers are usually cured using two kinds of peroxide catalyst: aroyl-peroxides and alkyl-peroxides [11, 12]. Aroyl-peroxides are used when the vulcanization process can be accomplished without pressure and they allow high reaction rates. Alkyl-peroxides are only used for vulcanization under pressure, as they do not form carbonic acids as decomposition products [1, 12]. Liquid silicone rubbers (LSR) have the same structure as solid silicone rubbers. However, the chain length of the polydimethylsiloxane used for LSR is lower by a factor of about 6. Therefore, the viscosity of the polymer is reduced by a factor of about 1,000 [1, 3, 12]. The curing of liquid silicone rubber is almost exclusively carried out with a platinum-catalyzed hydrosilylation reaction, which does not generate by-products [9, 12]. Because of their low viscosity, LSR can be pumped through pipelines and tubes to the cure equipment. Two components are pumped to a static mixer by a metering machine were the curing process may start taking place; loss of material in the feed lines is avoided using cold runners [9]. Injection molding is one of the preferred methods to process liquid silicone rubbers. Even though these machines can be expensive, they can be fully automated, not requiring human intervention during the process, resulting in higher quality parts and product consistency [9, 13]. It is during the injection molding of the LSR polymer and the subsequent vulcanization process that the final viscoelastic properties of the silicone part are set. Depending on the final degree of cure, the consistency and homogeneity of cure, which in turn depend on the quality of the thermal layout of the mold and runner system, a part's final properties may or may not be adequate for its final application and function.

The mechanical behavior, particularly the viscoelastic response of silicone rubber parts is of extreme importance to fulfill their function in a finished product. Depending on the application, one is interested in the response of the material in large time scales, from e.g. 1 second for mechanical loading, down to 0.0001 seconds for sound transmission or absorption, equivalent to frequencies between 1 and 10,000 Hz, respectively. In this paper, we present measurements and modeling of the vulcanization process of LSR during processing, looking into the exothermal reaction of curing, the rheology and viscosity development during heating and curing and the formation of the viscoelastic properties as the material makes a transition from a viscous fluid to a viscoelastic solid. Finally, this paper presents the viscoelastic properties of a fully cured LSR and shows how time-temperature superposition can be used to present properties at low as well as high excitation frequencies, reflecting the behavior from mechanical loading to transmission of sound, respectively.

VULCANIZATION OF LSR

The mechanism for crosslinking of elastomers and thermosets is very complex because of the relative interaction between the chemical kinetics and the changing of the physical properties [14]. In order to capture the cross-linking during vulcanization a semi-empirical phenomenological approach was selected for this research because even though the individual steps of the curing process of silicone rubber can be found in literature [1 – 4, 12], none have a kinetic model that describes the crosslinking process in real processing conditions.

The curing process can be described as the reaction between the two chemical groups denoted by *A* and *B,* which link two segments of a polymer chain. The reaction can be followed by tracking the concentration of unreacted *A*s or *B*s, C_A or C_B. The degree of cure can be then defined as follows [5, 6, 13, 14],

$$c = \frac{C_{A,0} - C_A}{C_{A,0}}, \qquad (1)$$

where $C_{A,0}$ is the initial concentration of *A*. The degree of cure is zero when there has been no reaction and equals one when all *As* have reacted and the reaction is complete. It is difficult to physically monitor reacted and unreacted *A*s and *B*s during the reaction without costly spectroscopy analysis. However, the degree of cure can be related to the heat released during the reaction because the curing of elastomers is an exothermic process. The energy released in the exothermal reaction is proportional to the cross-linked bonds formed, as it can be said that each bond releases the same amount of energy [5 – 8]. Therefore, heat released during vulcanization can be calculated using,

$$Q = \int_0^t \dot{Q}\,dt, \qquad (2)$$

where Q is the heat released up to time t and $\dot{Q}$ is the instantaneous rate of heat released by the sample. The total heat of reaction, Q_T, is therefore equal to,

$$Q_T = \int_0^{t_{final}} \dot{Q}\,dt, \qquad (3)$$

where t_{final} is the time at which the reaction is complete. The reaction rate, dc/dt, can then calculated as,

$$\frac{dc}{dt} = \frac{\dot{Q}}{Q_T}. \qquad (4)$$

The degree of vulcanization is obtained by integration of equation (4),

$$c = \frac{Q}{Q_T}. \qquad (5)$$

Within this research the kinetics of cure were modeled using the nth-order Kissinger [15, 16] and the (n+m)th-order auto-catalytic Kamal-Sourour models [17, 18], following the work of Hernandez-Ortiz and Osswald [13, 19].

The challenge of modeling the curing is to take information from the differential scanning calorimeter (DSC) and find the parameters for the kinetic models. Hernandez-Ortiz and Osswald [11, 19] developed a technique to use the Kamal-Sourour model to fit dynamic DSC data [27].

A liquid silicone rubber, denoted as LSR and a solid silicone rubber, expressed as HCR, were analyzed via thermal analysis to determine the progression of the curing processes, using the methodology of Hernandez-Ortiz and Osswald [10,11, 19]. The specific properties being studied were peak temperature, heat of reaction, and extent of reaction. A Differential Scanning Calorimeter equipment manufactured by Netzsch (Phox DSC 200 PC) was used to measure the heat of reaction for the samples. Sealed aluminum pans were used to analyze all reactions. The mass of the samples ranged from 10 mg to 30 mg. A sealed empty pan was used as a reference. The total heat of reaction was measured by a dynamic scan from 20°C to 150°C using heating rates of 1.0, 2.5, 5.0, and 10.0 K/min. Multiple scanning rates were used to gain insight into the effect of time and temperature on the vulcanization reaction. Repeatability was obtained for each heating rate. All experiments were performed under nitrogen purge.

The autocatalytic Kamal-Sourour model used to model the cure kinetics is defined as follows [17, 18],

$$\frac{dc}{dt} = \left(k_1 + k_2 c^m\right)\left(1 - c\right)^n, \qquad (6)$$

where m and n are the reaction orders and k_1 and k_2 are the rate constants described by the Arrhenius equation, i.e.

$$k_i = a_i \exp\left(\frac{E_i}{RT}\right) \qquad (7)$$

The six parameters in the model (a_1, a_2, E_1, E_2, m, and n) can be fitted to the experimental DSC data via a least-squares estimation algorithm developed by Marquardt [28, 29]).

The Hernandez-Ortiz and Osswald technique uses one or more dynamic DSC scans, avoiding the problems that arise by using isothermal DSC data.

Figure 1 shows the experimental cure rates and fitted Kamal-Sourour model cure rates for Liquid Silicone Rubber at heating rates from 1 K/min to 10 K/min. The figure illustrates the good performance of existing models and the non-linear fitting technique to predict the curing rate of vulcanizing LSR.

In contrast HCRs present lower repeatability than LSRs, because the HCR is pre-vulcanized up to a certain degree of cure before storing. During storage, it continues to crosslink at different proportions, depending on the location within the block. Furthermore, to finish cure of an HCR during the process, higher temperatures must be used and lower curing rates are achieved. To illustrate the difference between the two types of silicone rubbers Figure 2 presents the curing rates of an LSR and a HCR [13]. From the figure it is clear that HCR requires processing temperatures of 100K higher than those required when processing LSR. Furthermore, Figure 2 also illustrates that the curing rates achieved with LSR are 5 times higher than those achieved with HCR, leading to much shorter cycle times.

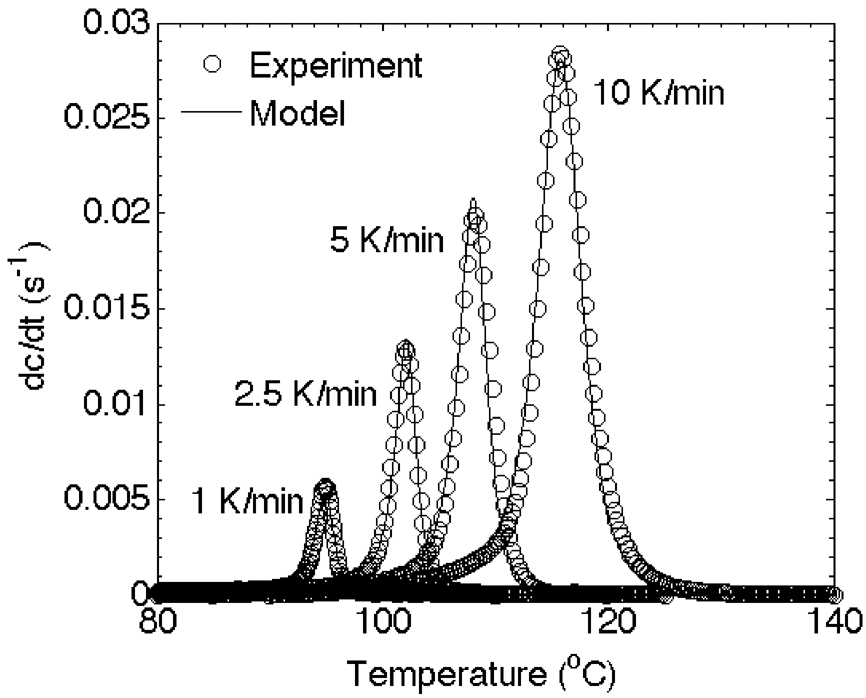


Figure 1 – Fitted model and experimental data for a LSR resin

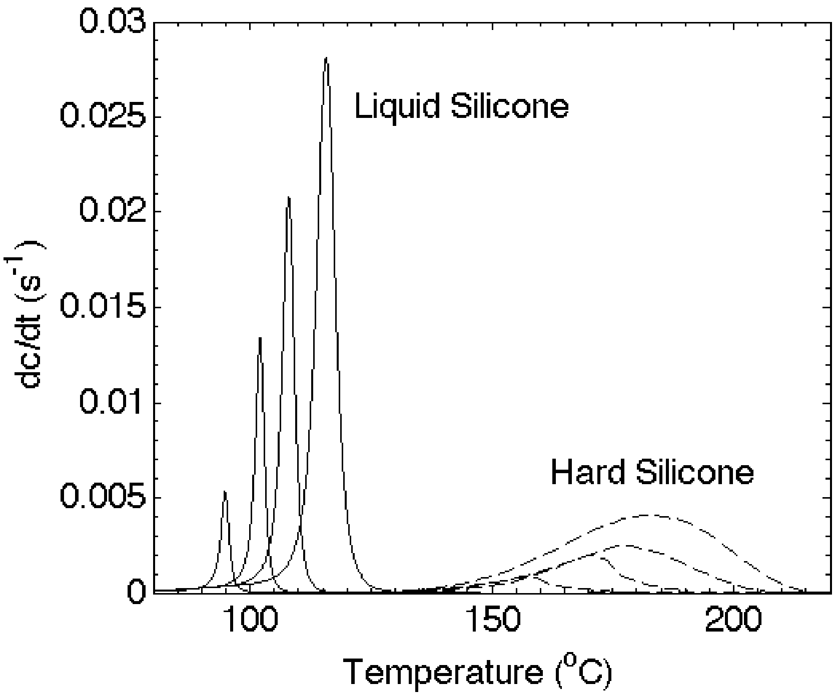


Figure 2 – Comparison of cure rate of LSR and HCR

DEVELOPMENT OF VISCOELASTIC PROPERTIES DURING VULCANIZATION

Any polymeric material's mechanical or rheological behavior is governed by both, elastic and viscous responses. When subjecting a purely elastic material, also referred to as a Hookean solid, to a sinusoidal strain input defined by

$$e = e_0 \sin(wt). \qquad (8)$$

the stress response will be in phase with the strain input and will have the form

$$s = s_0 \sin(wt). \qquad (9)$$

If we define the modulus as the ratio of the stress and the strain, the resulting value is a constant given by

$$E = \frac{s_0 \sin(wt)}{e_0 \sin(wt)} = \frac{s_0}{e_0}. \qquad (10)$$

On the other hand when subjecting a purely viscous material, referred to as a Newtonian fluid, to the same strain input, the stress response will be in phase with the strain rate, thus allowing us to define the viscosity using

$$\eta = \frac{\sigma_0 \cos(\omega t)}{\dot{\varepsilon}_0 \cos(\omega t)} = \frac{\sigma_0}{\dot{\varepsilon}_0}. \qquad (11)$$

Since the stress response of a Newtonian fluid can also be written as

$$\sigma = \sigma_0 \sin(\omega t + \frac{\pi}{2}) \qquad (12)$$

Here, it can be said, that the stress response is lagging the strain input by 90° or $\frac{\pi}{2}$ radians. For polymeric materials, the stress response is somewhere between the elastic and liquid responses, and can be expressed using

$$\sigma = \sigma_0 \sin(\omega t + \delta) \qquad (13)$$

where, δ is the loss angle, caused by damping – or viscous response – within the elastic behavior of the molecular structure measured with a dynamic mechanical analyzer (DMA) or a cone–and–plate viscometer. For this viscoelastic material the ratios of stress to strain, and stress to strain rate, are no longer straight forward, and lead to the so-called *complex modulus*, E^*, and *complex viscosity*, η^*, respectively. Taking the data acquired with a DMA, the complex modulus becomes

$$E^* = \frac{\sigma_0 \sin(\omega t + \delta)}{\varepsilon_0 \sin(\omega t)} = \frac{\sigma_0 \sin(\omega t)\cos(\delta)}{\varepsilon_0 \sin(\omega t)} + \frac{\sigma_0 \cos(\omega t)\sin(\delta)}{\varepsilon_0 \sin(\omega t)} = E' + E'' \qquad (14)$$

where, E' is the elastic portion of the complex modulus, referred to as the *storage modulus*, and E'' the viscous portion, referred to as the *loss modulus*. It is clear that when the loss angle δ is less than $\pi/4$ the polymer behaves like a viscoelastic solid ($E' > E''$), and when it is greater than $\pi/4$ it behaves like a viscoelastic liquid ($E' < E''$). Hence, we can define the transition between solid and liquid, such as the gel point during vulcanization, at the point when $\tan(\delta) = 1$.

The measurements performed with a viscometer can be used to compute the complex viscosity using

$$\eta^* = \frac{\sigma_0 \sin(\omega t + \delta)}{\dot{\varepsilon}_0 \cos(\omega t)} = \frac{\sigma_0 \sin(\omega t)\cos(\delta)}{\dot{\varepsilon}_0 \cos(\omega t)} + \frac{\sigma_0 \cos(\omega t)\sin(\delta)}{\dot{\varepsilon}_0 \cos(\omega t)} = \eta' + \eta'' \qquad (15)$$

where, η' is the elastic portion of the complex viscosity, referred to as the *storage viscosity*, and η'' the viscous portion, referred to as the *loss viscosity*. It is obvious that regardless of the measuring equipment, there is a direct relation between the complex modulus and the complex viscosity given by

$$E' = \eta'' \omega \qquad (16)$$

and

$$E''=h'w \qquad (17)$$

for elongational deformation, and

$$G'=h''w \qquad (16)$$

and

$$G''=h'w \qquad (17)$$

for shear.

Hence, if we return to the vulcanizing LSR of the previous section, and measure the viscosity as a function of time using a heating rate of 10K/min the behavior begins with a loss shear modulus below the storage shear modulus (Figure 3). The measurements were performed with a cone-plate rheometer from TA Instruments, model ARES G2. The chosen diameter was 25 mm, the strain 0.5 % and the force 1 N. In the graph we can see that as the material begins to heat, the viscosity (loss) drops somewhat. However, as the cross-linking reaction kicks-in, the viscosity (loss) as well as the modulus (storage) rise. The elastic component rises at a somewhat higher rate, and at about 48^{o}C becomes higher than the loss term. This is when the vulcanizing LSR reaches its gel point and makes a transition from liquid to solid behavior.

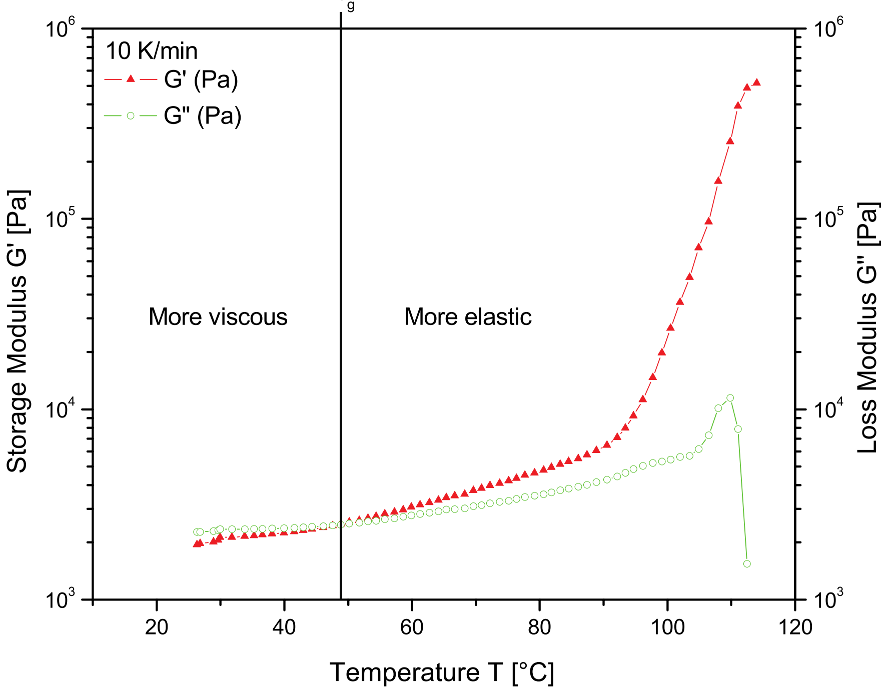


Figure 3 – Complex modulus of a LSR during vulcanization

If we only regard the viscous terms, we can plot the viscosity as a function of temperature or time as shown in Figure 4. Here, we can see various distinct effects. First, we see a drop of viscosity as the LSR's temperature rises leading to more free volume between the molecules. This facilitates the cross-linking reaction which results in a viscosity increase which marks the second phase of the reaction. Furthermore, the tests were performed at different frequencies. We can see that an increase in frequency leads to a drop in viscosity, reflecting the shear-thinning behavior, or the pseudo-plasticity of the LSR resin.

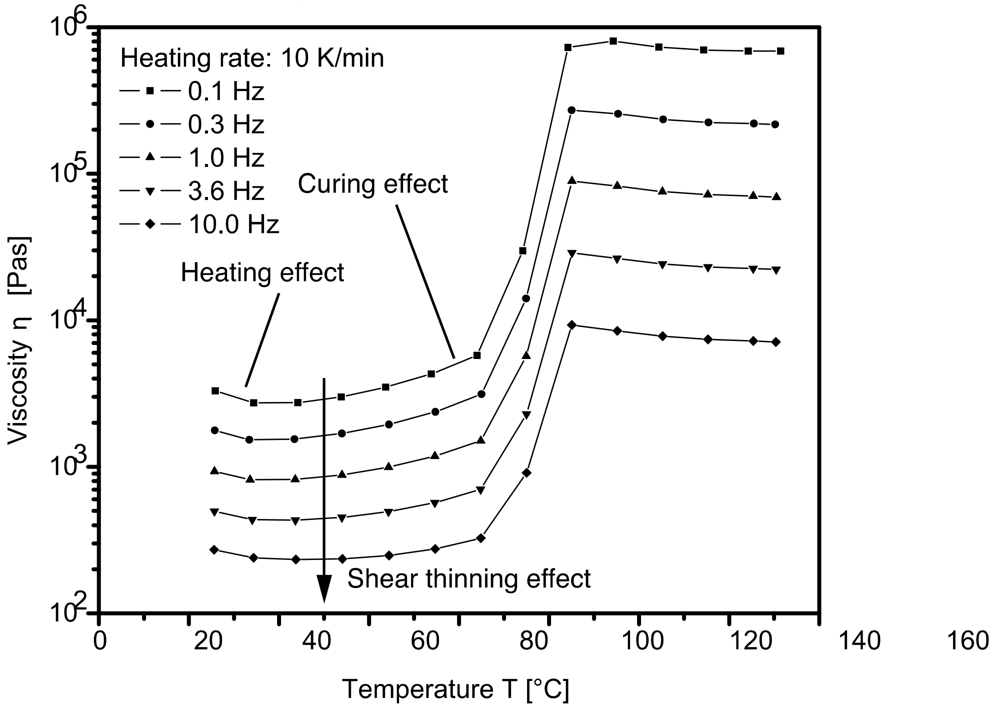


Figure 4 – Viscosity of an LSR during vulcanization measured at different frequencies

VISCOELASTIC BEHAVIOR OF VULCANIZED LSR

Once vulcanized, LSR has reached its final properties. These properties, in-turn, are a function of time and temperature. Figure 5 presents measurements of the storage modulus as a function of frequency for temperatures between 35°C and 105°C and frequencies between 1 and 100 Hz in a DMA from TA Instruments, model RSA III. First of all, it must be noted that, while a variation is reflected in the tests, the storage modulus is very stable when compared to other polymers and elastomers. It can be seen that as frequency increases from 1 to 100 Hz, the modulus also increases by a factor of 30 to 70% for 105°C and 35°C, respectively. The increase in modulus is a result of hindered stress relaxation effects at the higher frequencies or lower time scales; frequencies of 1 and 100Hz correspond to time scales of 1 and 0.01 seconds, respectively.

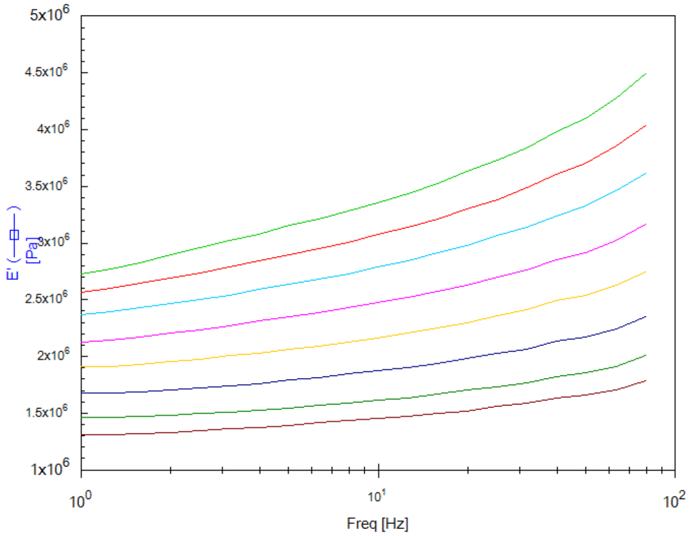


Figure 5 – Storage modulus as a function of frequency measured at various temperatures

Using the principle of time-temperature superposition the curves in Figure 5 can be shifted horizontally to generate curves over a larger range of frequencies. If we fix the curve that corresponds to 105°C and shift all other curves to match-up with this reference temperature (Figure 6) we extend the frequency from a maximum of a 100 Hz to a maximum of 10,000 Hz, equivalent to a time scale of 0.0001 seconds. In order to generate the master curve for the storage modulus at 105°C, the curves were shifted a specific distance to match up with each other. The horizontal shift, a_T, is referred to as the shift factor and can be represented using an Arrhenius fit described by

$$a_T = e^{\frac{E_0}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)} \qquad (17)$$

Figure 7 presents a comparison between the shift that resulted from generating the master curve and an Arrhenius fit.

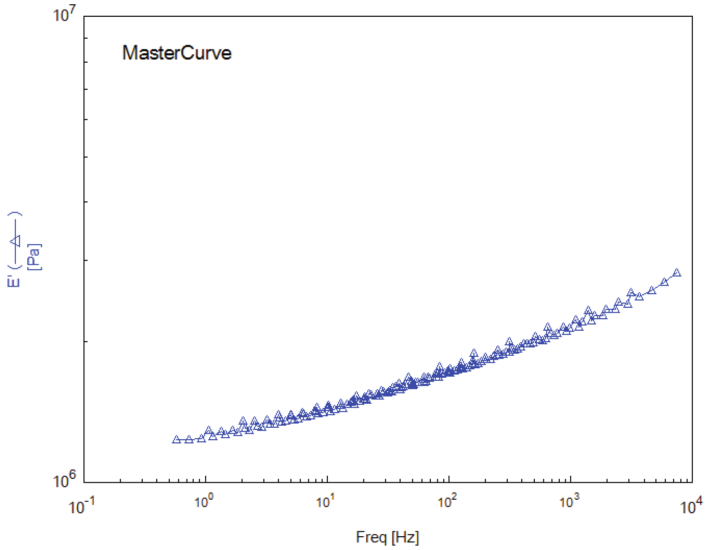


Figure 6 – Master curve for the storage modulus at 105°C

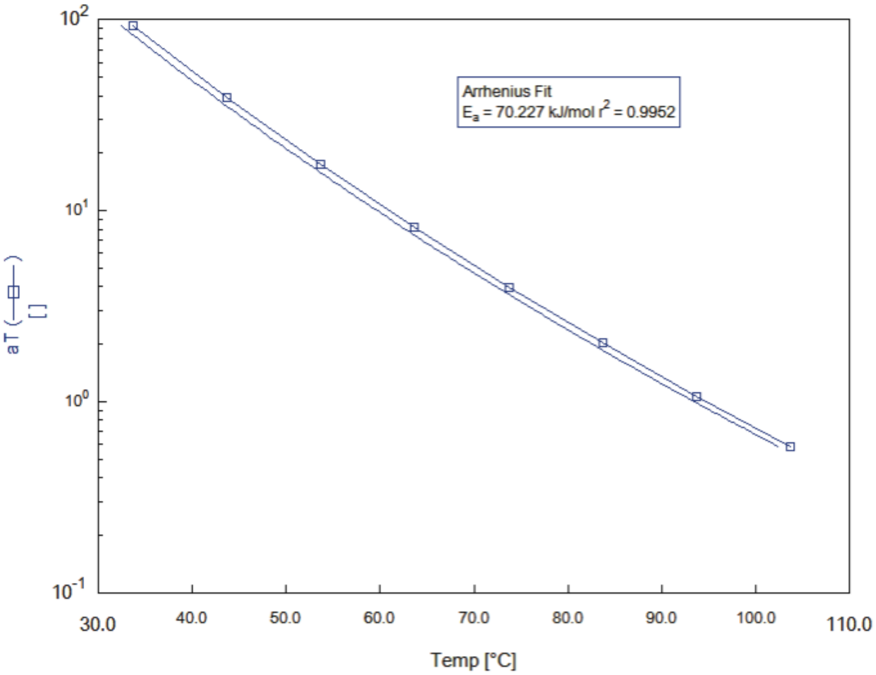


Figure 7 – Shift factor as a function of temperature compared to an Arrhenius fit

The master curve can now be shifted to describe the behavior of the LSR at any temperature such as the master curves for storage modulus, loss modulus and $tan\delta$ generated for a temperature of 95°C.

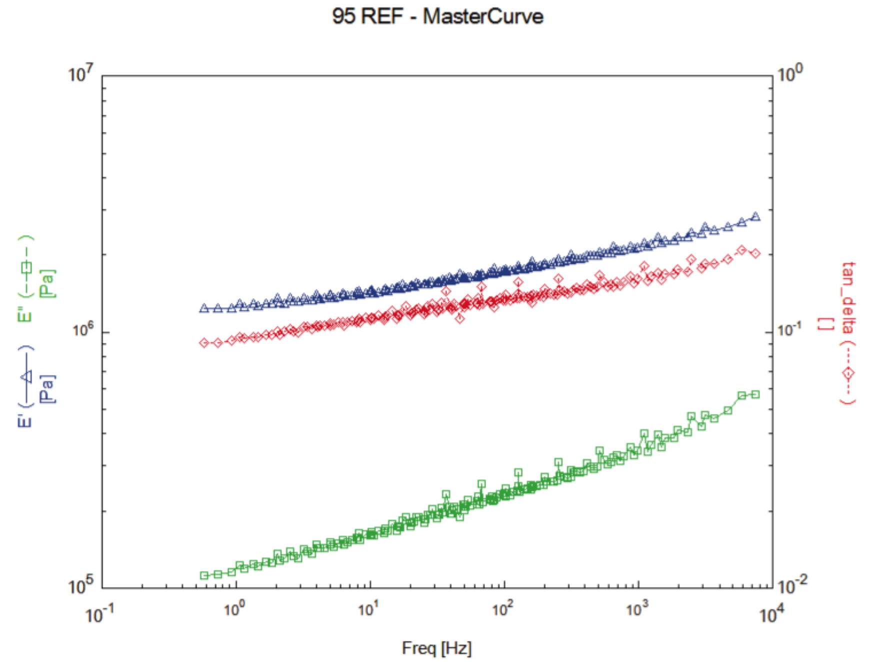


Figure 8 – Master curves for storage modulus, loss modulus and $tan\delta$ generated at 95°C

CONCLUSIONS

From DSC analyses of the vulcanization process we can conclude that processing LSR has best performance, quality control and less energy requirement than HCR processes. The main problem of HCR comes from its cure kinetics, needed for the pre-cured requirements of such processes. The accelerated kinetics at low temperatures of LSR, increases the processing performance, efficiency and control, which ensures that the final parts have a perfect consistency. It was also shown that curing has a profound effect on the viscoelastic performance of the cross-linking resins. Hence, full cure of the resin is indispensable to be able to achieve the required viscoelastic performance of the final product.

REFERENCES

[1] KOERNER, G., SCHULZE, M. and Weis, J. Silicones, Chemistry and Technology, Boca Raton, CRC Press, 1991.

[2] NOLL, W. Chemistry and Technology of Silicones, New York, Academic Press, 1968.

[3] TOMANEK, A. Silicones and Industry a Compendium for Practical Use, Munich, Wacker-Chemie Publisher, 1991.

[4] LYNCH, W. Handbook of Silicone Rubber Fabrication, London, Van Nostrand Reinhold Company, 1997.

[5] OSSWALD, T.A. and MENGES, G. Material Science of Polymers for Engineers, 2nd Edition, Munich, Hanser Publishers, 2003.

[6] YOUNG, R.J. and LOWELL, P.A. Introduction to Polymers, Great Brirain, 2000.

[7] OSSWALD, T.A., BAUR, E., BRINKMANN, S., OBERBACH, K. and SCHMACHTENBERG, E. International Plastics Handbook, Munich, Hanser Publishers, 2006.

[8] ODIAN, G. Principles of Polymerization, 3rd Edition, John Wiley & Sons, New York, 1991.

[9] LOPEZ, L. Modeling the Vulcanization of Liquid Silicone Rubbers, M.Sc. Thesis, Department of Mechanical Engineering, University of Wisconsin-Madison, Madison, 2004.

[10] COSGROVE, A., LOPEZ, L., HERNANDEZ-ORTIZ, J.P. and OSSWALD, T.A., SPE-ANTEC, Chicago, pp. 953, 2004.

[11] LOPEZ, L., COGROVE, A., HERNANDEZ-ORTIZ, J.P. and OSSWALD, T.A. Polym. Eng. Sci., vol. 47(5), pp. 675, 2007.

[12] Wacker-Chemie, The Grades and Properties of Elastisil® R Solid Silicone Rubber, Munich, 2001.

[13] OSSWALD, T.A. and HERNANDEZ-ORTIZ, J.P. Polymer Processing: Modeling and Simulation, Hanser Publishers, Munich, 2006.

[14] CALADO, V.M.A. and ADVANI, S.G. Thermoset Resin Cure Kinetics and Rheology, Chapter 2 of Processing of Composites by Dave, R.A. and Loos, A.C., Hanser Publishers, Munich, 2000.

[15] KISSINGER, H.E. Anal. Chem., vol. 49(11), pp. 1702, 1957.

[16] KISSINGER, H.E. J. Res. Natl. Bur. Stand., vol. 57, pp. 217, 1956.

[17] KAMAL, M.R. and SOUROUR, S. Polym. Eng. Sci., vol. 13(1), pp. 59, 1973.

[18] KAMAL, M.R. Polym. Eng. Sci., vol. 14(1), pp. 231, 1979.

[19] HERNANDEZ-ORTIZ, J.P. and OSSWALD, T.A. J. Polym. Eng., vol. 25(1), pp. 23, 2005.

[20] ENNS, J.B. and GILHAM, J.K. J. Appl. Polym. Sci., vol. 28, pp. 2567, 1983.

[21] WISANRAKKIT, G. and GILHAM, J.K. J. Appl. Polym. Sci., vol. 41, pp. 2885, 1990.

[22] HADIPRAJITNO, S. HERNANDEZ-ORTIZ, J.P. and OSSWALD, T.A. SPE-ANTEC, Nashville, pp. 818, 2003.

[23] JIA, Y., SUN S., XUE, S., LIU, L. and ZHAO, G. Polymer, vol. 43, pp. 7515, 2002.

[24] JIA, Y., SUN S., XUE, S., LIU, L. and ZHAO, G. Polymer, vol. 44, pp. 319, 2003.

[25] LOPEZ, L., OSSWALD, T.A. and WILICHOWSKI, P. SPE-ANTEC, Nashville, pp. 813, 2003.

[26] THERIAULT, R.P. Modeling and Simulation of the Manufacturing of Copper-Clar Laminates, Ph.D. Thesis, Department of Mechanical Engineering. University of Wisconsin-Madison, 1998.

[27] HERNANDEZ, H, and OSSWALD, T.A. *J. of Applied Pol. Sc.*, (119), pp. 1864, 2011.

Chapter 3

Multi-Component / Overmolded Parts

Multi-Component / Overmolded Parts

Multi-component or multi-material injection molding is a process that has developed greatly in the last decade. This process has grown not only due to technological advancements, but also due to OEMs' searching for new ways to gain advantage over competitors in product quality and value.

Multi-component molding may be described as the integration of multiple parts into one component directly in the molding process—a process that previously required separate manufacturing and assembly steps, but that has now been streamlined into a single multi-part solution.

There are many names for all the different multi-material injections molding processes, such as two-component (2K), overmolded, co-injection, or multi-component. We will refer to the process of making a part out of more than one material in the same manufacturing process simply as the multi-component process.

The main reason for a multi-component process is to reduce costly or complicated assembly steps—for example, assembling gaskets with complicated geometries—although there are many other benefits. When materials are overmolded (placed one over the other), you obtain a combination of the different properties of the materials used in the part. For example, when overmolding onto metals, you may be achieve the stiffness and shine of a metal but the softness, smoothness, and transparency of a liquid silicone rubber.

Another benefit of overmolding with LSRs is that grades have been developed to offer prime-less adhesion to a wide range of substrates, including metals and engineering plastics. Many materials require the use of primers or surface treatments, which leads to extra steps in the manufacturing process. LSRs, however, will bond to most surfaces through direct bonding. Due to the high compatibility between materials, full bond strength is obtained immediately after de-molding. Parts can be bonded through chemical and mechanical adhesion, leading to the strongest possible bond between materials. Other benefits for multi-component molding of LSRs include:

- The ability to mold complex designs and geometries, which could never be done by a separate assembly step.
- The possibility of integrating bonding and non-bonding materials to generate movable parts that otherwise could never be assembled in such a way.

- Superior surface finish with the best bonding characteristics.
- Clean surfaces and consistent thicknesses throughout the parts.
- Perfect alignment of seals, gaskets, or fittings, consistent for every part made.
- Competitive pricing by reducing assembly steps, production time, and material waste.

Chapter 4

Modeling the Vulcanization Process

Modeling the Vulcanization Process of High Consistency Rubber and Liquid Silicone Rubber

Amelia Cosgrove, Lina Lopez, Juan Hernandez-Ortiz, Tim Osswald
Polymer Engineering Center, Department of Mechanical Engineering
University of Wisconsin – Madison, WI 53706

Enrique Camacho
Simtec Silicone Parts, LLC

Abstract

A kinetic model of the vulcanization process of high consistency rubber (HCR) and liquid silicone rubber (LSR) was developed. The exothermal vulcanization process was measured with a differential scanning calorimeter. Viscosity was measured with a cone and plate rheometer. A computer program fit coefficients to the experimental data. Values for activation energy and fitted rate coefficient were found using both *n*th order polynomial and autocatalytic models. A kinetic model of vulcanization will help manufacturers understand and optimize their production processes.

Introduction

Silicone rubber has many applications. It is widely used in electronics, aerospace, consumer goods, and the medical industries. It maintains its mechanical properties over a range of temperatures, has good electrical conductivity, is easy to color, and comes in medical quality grades. Silicone rubber is a thermoset elastomer with a backbone of alternating silicone and oxygen atoms and methyl or vinyl side groups, as seen in Fig. 1. There are two types of silicone rubber, solid and liquid. The basic structure of the two types of silicone rubber is the same, but the cure and processing are radically different.

High Consistency Rubber (HCR) is produced in large batches. The components are mixed at high temperature, and a peroxide catalyst is added. Some cross-linking occurs, but the process is interrupted before vulcanization is complete. The lightly cross-linked silicone rubber is formed into sheets for shipping and storage. When the HCR is ready to be used, it is mixed with rollers and transfer molded. After the part is molded, it is transferred to an oven where post-vulcanization occurs.

Liquid Silicone Rubber (LSR) is a two-component system. Component A contains a platinum catalyst and component B contains methylhydrogensiloxane as a cross-linker and an alcohol inhibitor. The two components are stored separately and mixed during processing. LSR is processed with cold runner injection molding equipment.

During vulcanization, the long chains of the elastomer chemically cross-link. Each cross-linking releases a quantum of energy, making it an exothermic reaction. During this process, the catalyst creates bonds between the long chains, creating a three dimensional matrix. This network greatly improves the mechanical properties of the rubber. It is important to understand how silicone rubber vulcanizes in order to optimize the processing conditions and choose the correct material for each application.

DSC Measurement of Vulcanization

Vulcanization can be studied with a Differential Scanning Calorimeter (DSC). To take a measurement with a DSC, two small pans are placed in the DSC's heating chamber. One pan contains the material to be measured. An empty pan serves as a reference. Thermocouples underneath the pans measure the temperature. During a thermal sweep, the sample pan and the reference pan are maintained at the same temperature. The sample with the higher heat capacity will absorb a larger amount of heat, which is proportional to the difference between the heat capacity of the measured sample and the reference sample (1).

The energy released in the exothermal reaction is proportional to the cross-linked bonds formed and it is assumed that each bond releases the same amount of energy. The vulcanization of the sample is found by measuring the energy released as the sample is heated from below room temperature to well above the vulcanization temperature.

The heat released during vulcanization can be calculated by,

$$Q = \int_0^{\tau} \dot{Q} dt \quad (1)$$

where Q is the is the heat released up to time τ and $\dot{Q}$ is the change in heat of the sample. The total heat of reaction, Q_T, is therefore equal to,

$$Q_T = \int_0^{\tau-final} \dot{Q} dt \quad (2)$$

where τ-final is the time at which the reaction is complete. The reaction rate, *dc/dt*, is then calculated as,

$$\frac{dc}{dt} = \frac{\dot{Q}}{Q_T}. \quad (3)$$

The measured data is then fit to the theoretical model. The silicone vulcanization reaction can be described by an autocatalytic model. For an autocatalytic curing reaction, the Kamal-Sourour reaction model (2, 3) as shown in equation 4 is used.

$$\frac{dc}{dt} = \left(k_1 + k_2 c^m\right)\left(1 - c\right)^n \quad (4)$$

In equation 4, m and n are the reaction orders, c is the extent of the vulcanization reaction, defined by $c = {Q}/{Q_T}$, and k_1 and k_2 are the Arhenius overall constants defined by,

$$k_1 = a_1 \exp\left(\frac{-E_1}{RT}\right) \quad (5)$$

$$k_2 = a_2 \exp\left(\frac{-E_2}{RT}\right) \quad (6)$$

where a_i is the fitted rate coefficient, E_i is the activation energy, R is the universal gas law constant, and T is the vulcanization temperature.

It is not necessary to modify the constants of the reaction due to diffusion, because the materials vulcanize above their glass transition temperatures. For materials that vulcanize below the vitrification point, the model accurately predicts the total process. This is due to the fact that while performing the test above the glass transition temperature there is sufficient free volume between the molecules to allow for freedom of movement during the molecular cross-linking process, and therefore diffusion does not play a large role.

The six parameters from the Kamal-Sourour model that need to be fitted to the experimental data can represented as an unknown vector quantity, via a least-squares estimation algorithm developed by Marquardt (4).

$$X = \{m\ n\ a_1\ E_1\ a_2\ E_2\} \quad (7)$$

The parameters then are expanded into a power series with temperature (T) as the independent variable (5)

$$x_i = a_{i1} + a_{i2}T + a_{i3}T^2 + O(T^3) \quad (8)$$

where i=1,…,6 and a_{ij} are the new goal of the fitting.

Experimental Procedures

Differential scanning calorimeter equipment manufactured by Netzsch (DSC 200 PC) was used to measure the heat of reaction for the samples. Sealed aluminum pans were used to contain all reactions. The mass of the samples used ranged from 10 mg to 30 mg. An empty pan was used as a reference. The total heat of reaction was measured by a dynamic scan using heating rates of 1, 2.5, 5, and 10 K/min. Multiple scanning rates were used to gain insight into the effect of time and temperature on the vulcanization reaction. Repeatability was obtained for each heating rate. All scans were performed under nitrogen purge. The A and B components of the liquid silicone rubber were mixed with a Mixpac (DMA 50) 1:1 static mixer using a Kenics mixing chamber. A 1:10 ratio of Sylgard 184 curing agent to elastomer was used for the PDMS.

Results

Repeatability was obtained for the DSC data. The model fitting was performed for the LSR and HCR at each vulcanization rate. As can be seen in Figs.2 through 5, the DSC data corresponds well with theory. The total heat of reaction and the peak temperatures for each material are included in Table 1. Experimental data and fitted models are graphed together for LSR and HCR in Figs. 6 and 7. The relationship between the LSR and PDMS can be seen in Fig. 5.

The corresponding values of m, n, a_1, E_1, a_2, and E_2 for LSR and HCR are summarized in Tables 1 and 2, respectively. The peak temperature for the three materials at all scan rates can be seen in Table 3.

Conclusion

The vulcanization reactions of LSR and HCR, as well as PDMS were measured using the DSC. The modified Kamal-Sourour model was utilized to identify the vulcanization reaction of liquid and solid silicone rubber from dynamic DSC experimental data. A set of vulcanization kinetics parameters was obtained using a non-linear least squares Levenberg-Marquardt algorithm. The developed model resulted in good agreement between the experimental data and the predictions. Further work is being done to fit other models to the vulcanization reaction of silicone rubber materials.

Acknowledgements

The authors would like to thank Simtec Silicone Parts for their support of this project. This research is partially supported by the National Science Foundation grant (DMI-0116415).

References

1. Osswald, T. A., Menges, G., Material Science of Polymers for Engineers, 2st Edition, Hanser/Gardner (2003)
2. Kamal, M.R. Polymer Engineering and Science, 14 (1), 231 (1979).
3. Kamal, M.R., Sourour, S. Polymer Engineering and Science, 13 (1), 59 (1973).
4. Marquart, D.W., Journal of Soc. Ind Applied Math, 11(2), (1963)
5. Hernandez-Ortiz, J.P., Osswald, T. A. UW Polymer Engineering Center, unpublished research (2003)

Table 1. LSR. Fitted values using a 5 K/min scan.

Parameter	O(1)	O(T)	$O(T^2)$
m	7.4140E+01	-7.0540E-02	-3.5051E-04
n	-1.5130E+00	-3.3828E-03	2.7015E-05
a_1	7.8546E+01	-4.6229E-01	6.8078E-04
E_1	5.3011E+04	6.3376E+00	-2.8889E-01
a_2	3.4989E+01	2.7318E-01	2.2352E-04
E_2	-1.3530E+05	1.1428E+02	8.7977E-01

Table 2. HCR. Fitted values using a 5 K/min scan.

Parameter	O(1)	O(T)	$O(T^2)$
m	8.4455E+01	-5.5926E-01	9.0122E-04
n	2.0456E+01	-1.0317E-01	1.2983E-04
a_1	1.6682E-22	-7.1679E-21	1.8524E-23
E_1	1.1447E+05	-6.5515E+02	2.1787E-01
a_2	-1.5320E+03	6.6209E+00	-7.1566E-03
E_2	-2.2411E+05	1.4717E+01	1.0666E+00

Table 3. Total Heat of Reaction and Peak Temperature

Material	Heating Rate (K/min)	Peak Temperature (°C)
HCR	1	157.7
	2.5	170.6
	5	177.6
	10	183.3
LSR	1	73.4
	2.5	81.7
	5	91.2
	10	95.9
PDMS	2.5	82.0
	5	90.5
	10	100.8

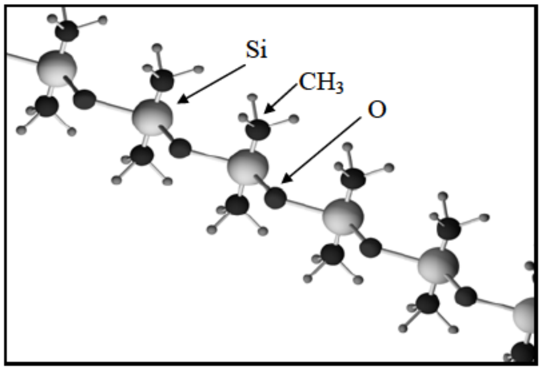


Figure 1. Molecular Structure of Silicone Rubber

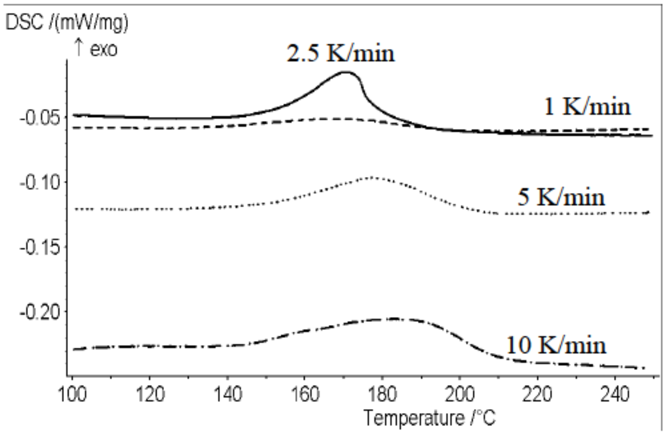


Figure 2. Dynamic Scans of HCR

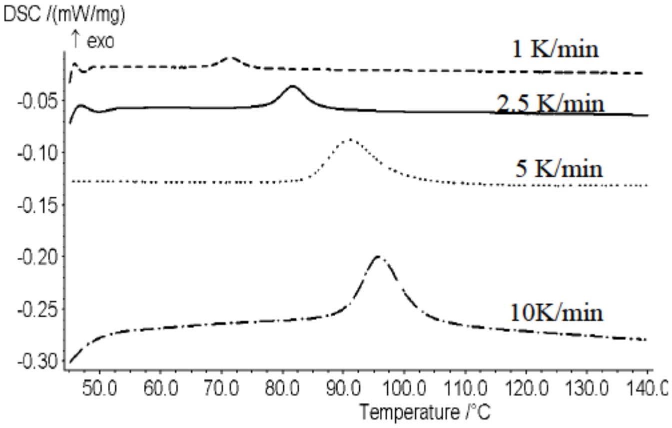


Figure 3. Dynamic Scans of LSR

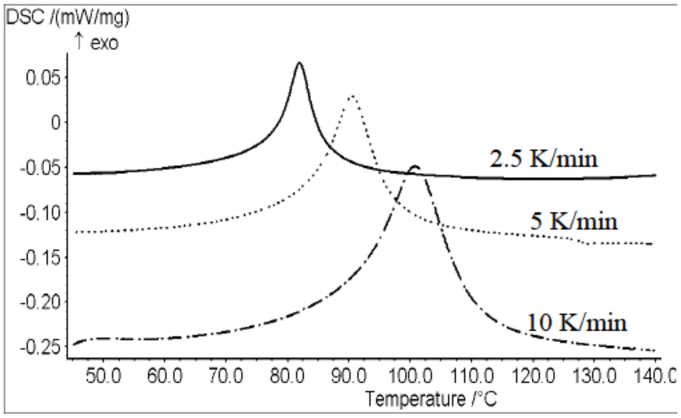


Figure 4. Dynamic Scans of PDMS

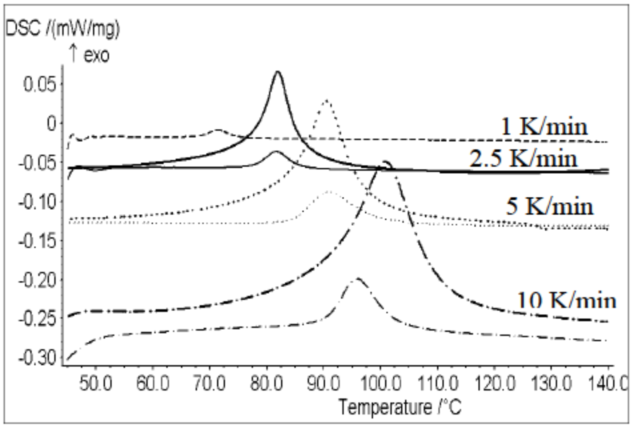


Figure 5. Comparison of Dynamic Scans of LSR and PDMS

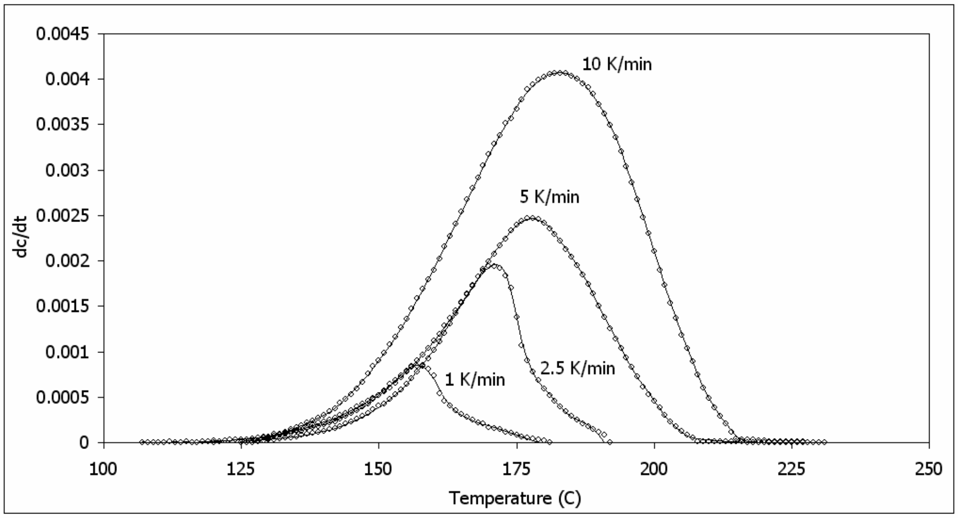


Figure 6. Fitted Model and Experimental Data for HCR

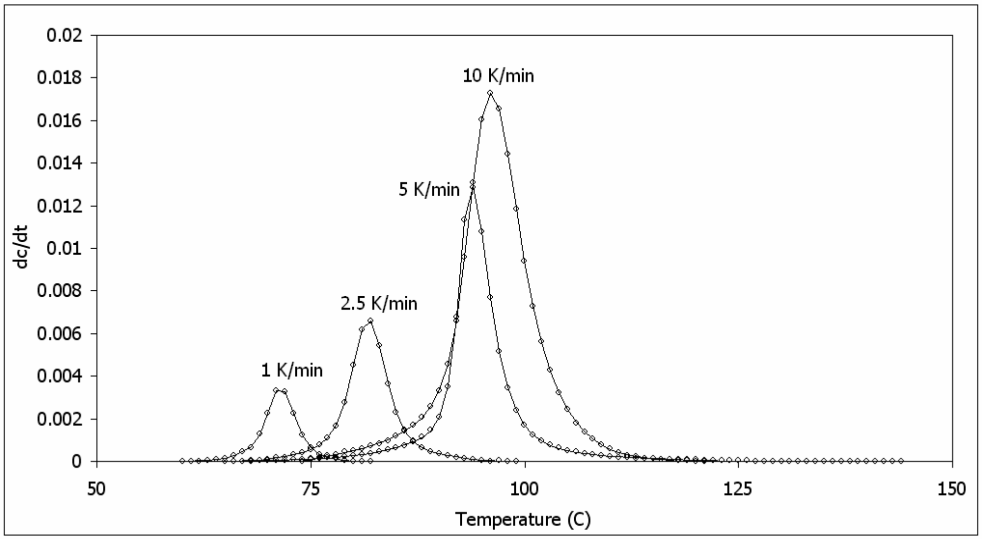


Figure 7. Fitted Model and Experimental Data for LSR

Chapter 5

Characterization and Modeling of the Curing Process of LSR

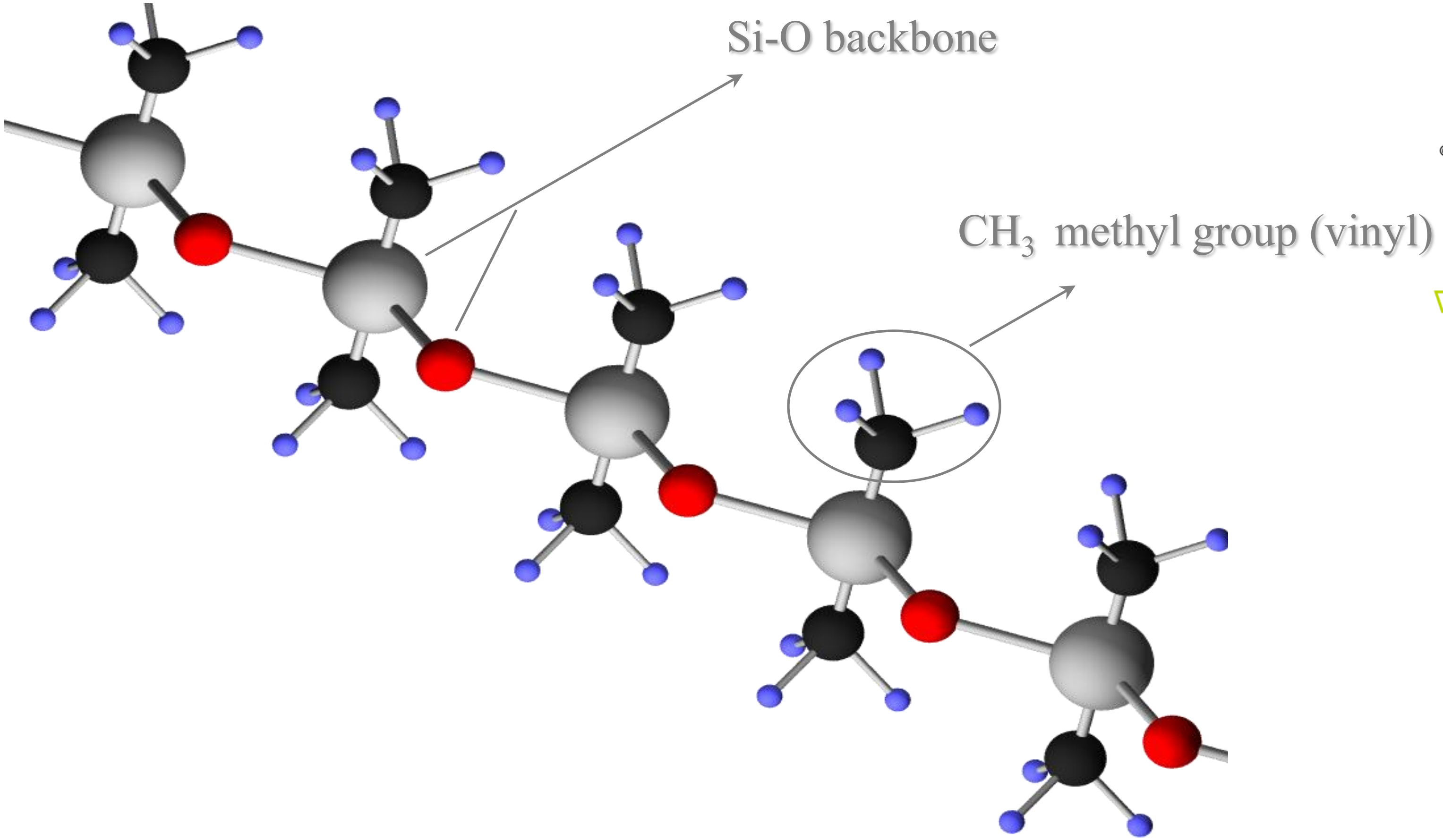
Characterization and Modeling of the Curing Process of Silicone Rubber

Enrique Camacho
Juan P. Hernandez-Ortiz
Professor Tim A. Osswald

Polymer Engineering Center
University of Wisconsin - Madison

simtec® SILICONE PARTS
AN ISO 9001 & 13485 CERTIFIED COMPANY

Silicone Rubber: Chemical Composition



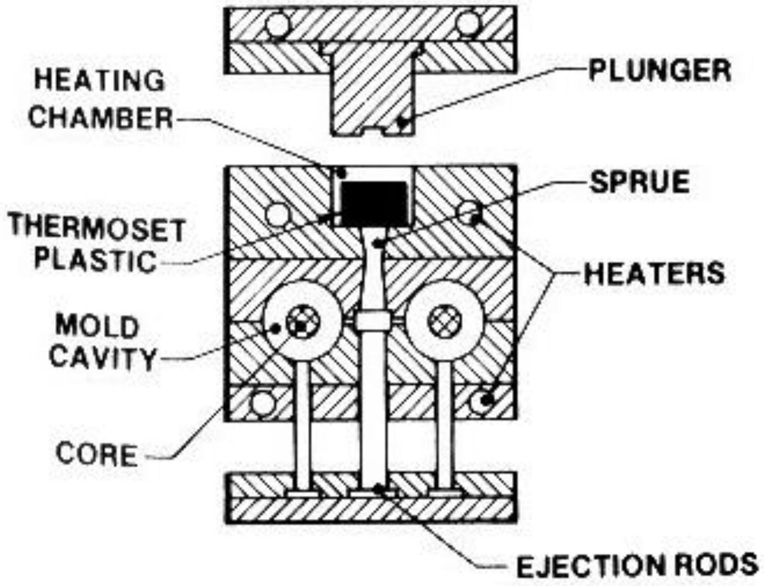
Si-O backbone

CH_3 methyl group (vinyl)

Hard Silicone Rubber (HSR)

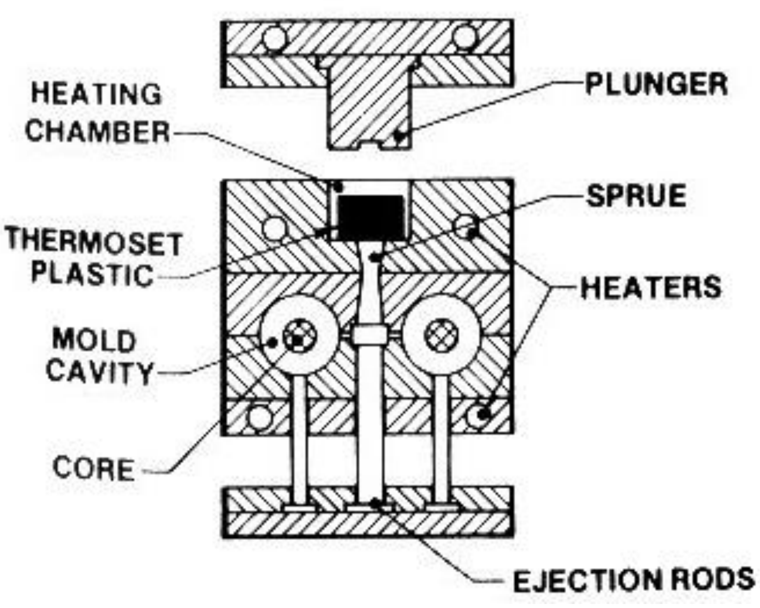
- Mixing of components at high Temperatures
- Peroxide as a catalyst
- Interruption of curing
- Partially cure sheets (aging)

Transfer Molding



Hard Silicone Rubber (HSR)

Transfer Molding



- Transfer molded into parts
- Post Processing
  - Flash removal
  - Post-cure baking

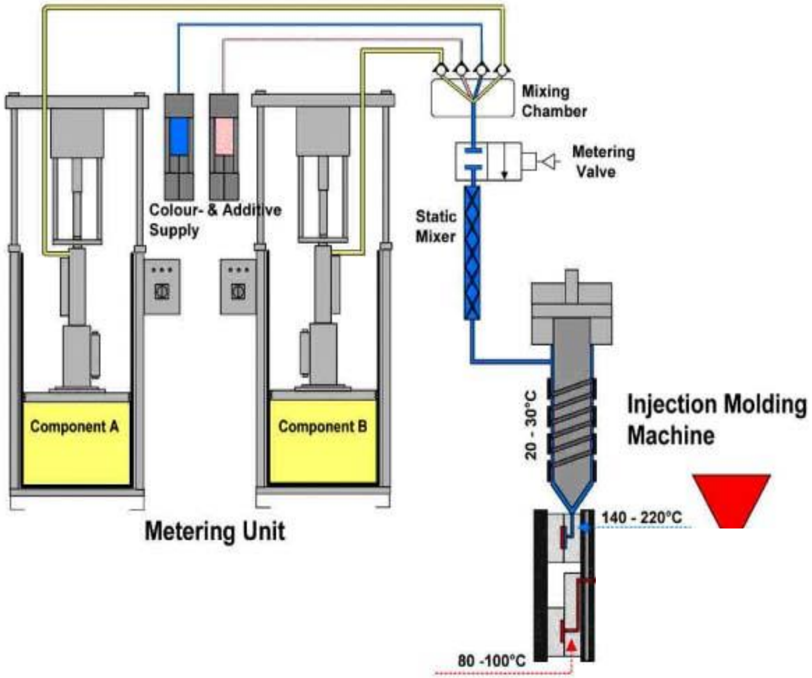
SILICONE PARTS

AN ISO 9001 & 13485 CERTIFIED COMPANY

Where Science Meets Innovation™

Liquid Silicone Rubber (LSR)

- Platinum as a catalyst
- Cold runner injection molded
- Precise Mixing
- Precise parts
- No post-curing
- All curing occurs in mold (no aging)
- Repeatable rate of cure



Objective

- Characterize the liquid

  - Thermal properties (specific heat capacity)
  - Cure reaction kinetics (heat of reaction, cure rate,…)
  - Rheological properties

- Modeling the cure process

  - Find a correct cure reaction model
  - Numerically find the reaction parameters
  - Coupling with FEM for process optimization

SILICONE PARTS

AN ISO 9001 & 13485 CERTIFIED COMPANY

Wacker Silicone: ELASTOSIL® LR

- 3088/20
  -Injection Molding: excellent molding, short cycle times
  -Self-lubrication after processing
  -Electrical connector seals and automotive applications

- 3088/30:
  -Minimum flash, high consistency quality
  -Self-lubricating
  -All-weather connectors, seals of individual conductors-good chemical resistance
  -Flexibility between -40ºC and 180ºC

GE Bayer: Baysilone®, Silopren®

- 2050:
  - -Transparent, easy to color
  - -high tensile strength
  - -connector inserts, seals, valve parts, masks, camera parts, rollers

- 2060:
  - -High thermal stability, excellent dielectric behavior, good elastic properties, long shelf life
  - -seals, stoppers, diaphragms, keypads, catheters, respiratory devices.

AN ISO 9001 & 13485 CERTIFIED COMPANY

Where Science Meets Innovation™

Cure Kinetics

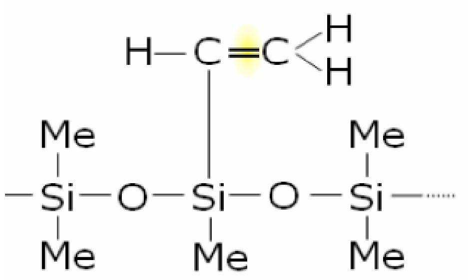
- Can be described by the reaction of two chemical groups denoted by A and B

- However, it is difficult to monitor reacted and un-reacted As and Bs during the curing reaction

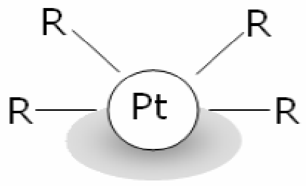
- Every cross-linking that occurs during a reaction releases a small amount of energy (heat)

- Exothermic heat released during cure can be utilized to monitor the degree of cure

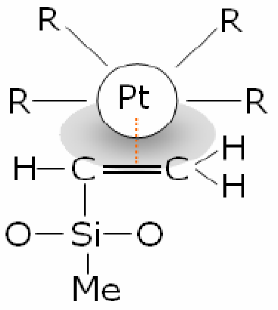
Reaction with Platinum Catalyst



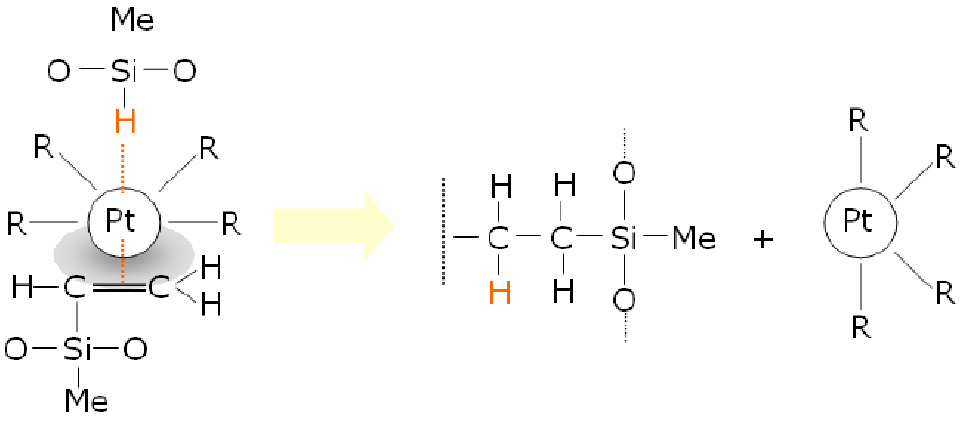
The vinyl double bond is reactive



The platinum center has one free coordination site



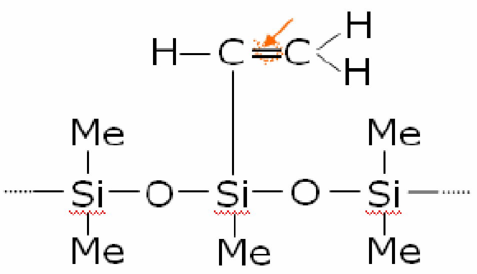
Interaction with the platinum center activates the double bond



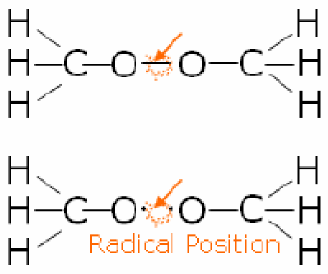
The vinyl group crosslinks by transforming the double bond, creating a single bond to a polymer chain; in this case, to a crosslinker molecule containing Si-H groups. The catalyst becomes free and is again available for further crosslinking.

AN ISO 9001 & 13485 CERTIFIED COMPANY

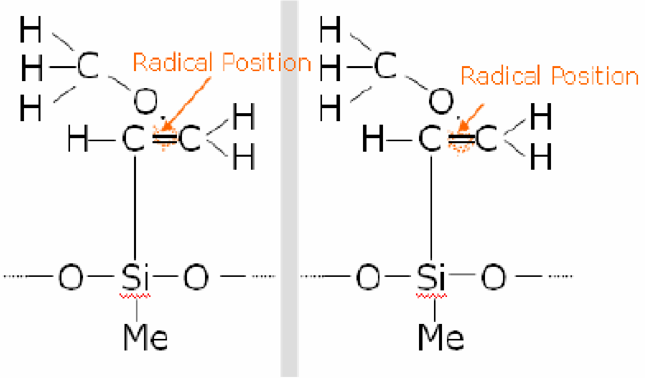
Reaction with Peroxide Catalyst



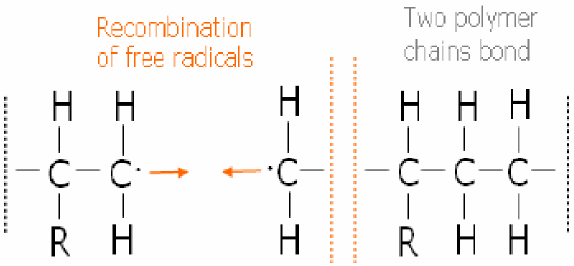
The vinyl double bond is reactive



The peroxide group produces an oxygen free-radical

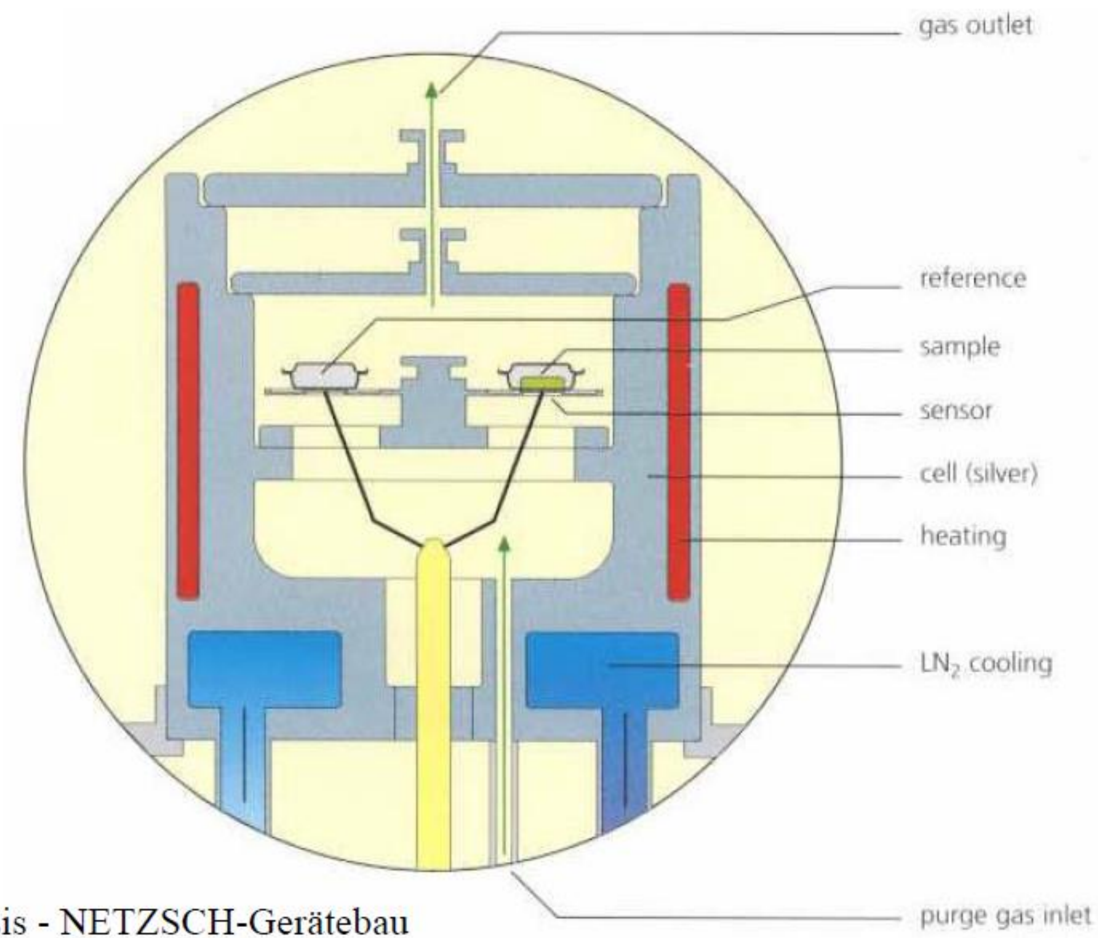


A reactive free radical is formed on the vinyl group



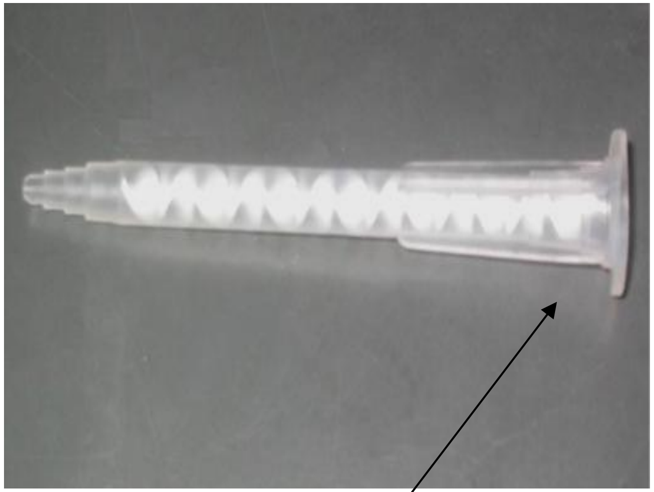
The free radical attaches itself to another polymer and forms a bridge. The free radical chain reaction then continues.

Differential Scanning Calorimeter (DSC)

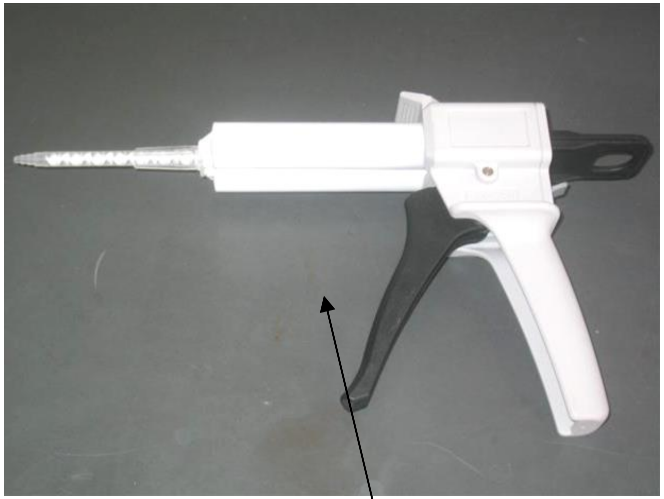


Netzsch Thermal Analysis - NETZSCH-Gerätebau

Mixing of Components



Static Mixer with 13 elements

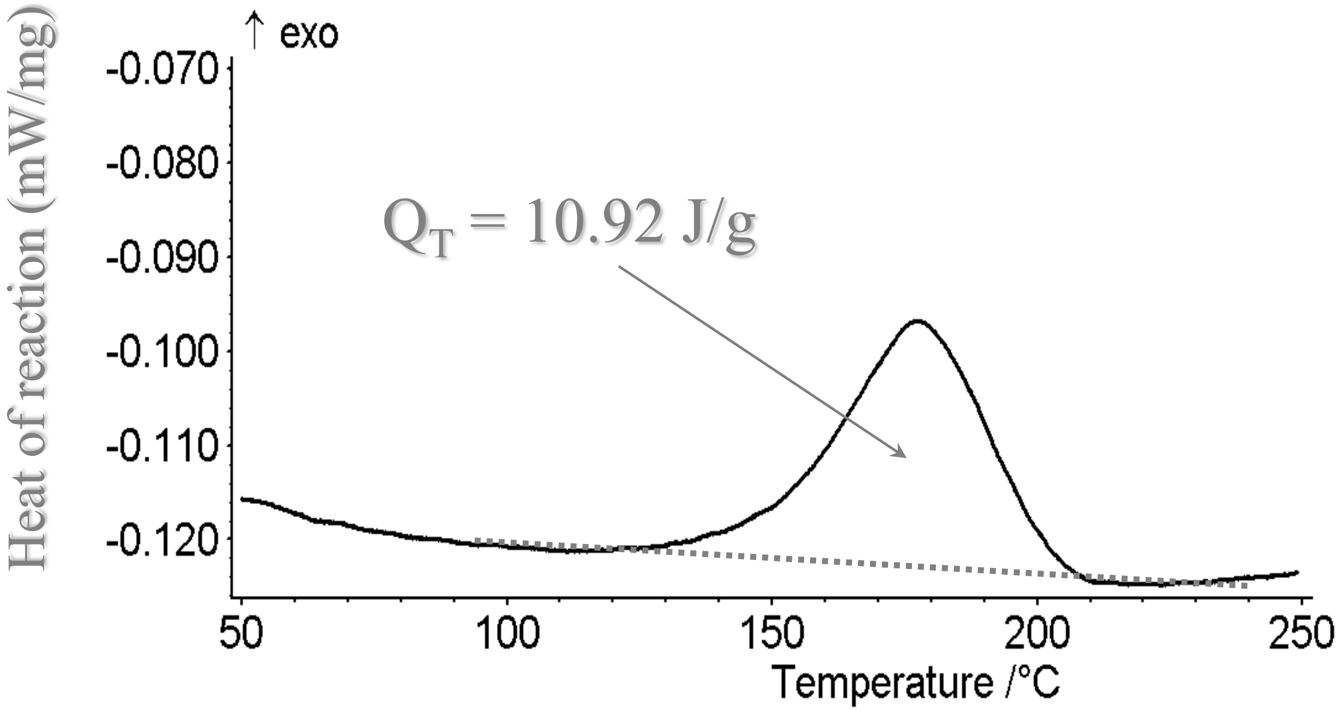


Mixing Components

AN ISO 9001 & 13485 CERTIFIED COMPANY

Where Science Meets Innovation™

Dynamic DSC Scan: 5K/min

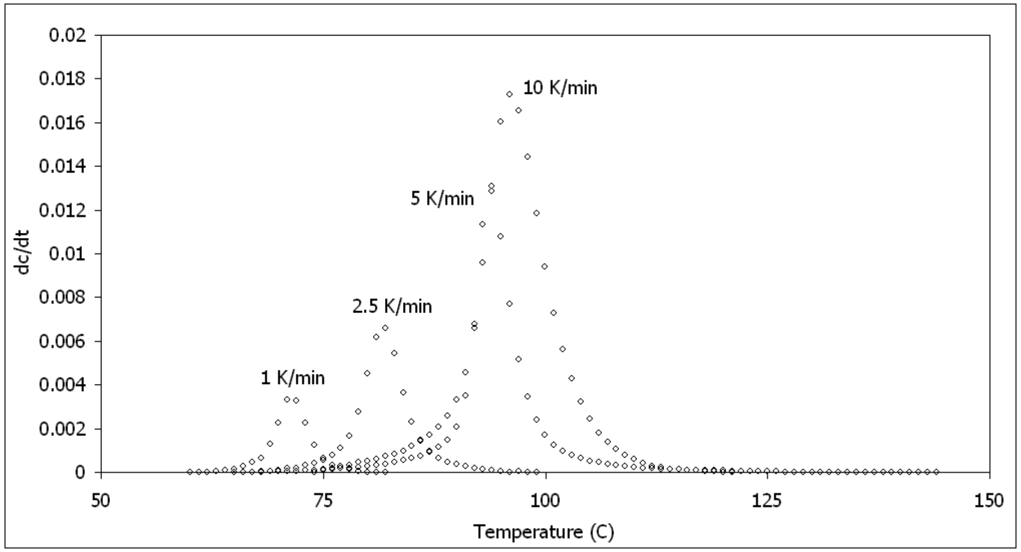


Cure degree: $c = \dfrac{Q}{Q_T}$

Cure rate: $\dfrac{dc}{dt} = \dfrac{\dot{Q}}{Q_T}$

AN ISO 9001 & 13485 CERTIFIED COMPANY

Numerical Fitting: Kamal-Sourour + Kissinger

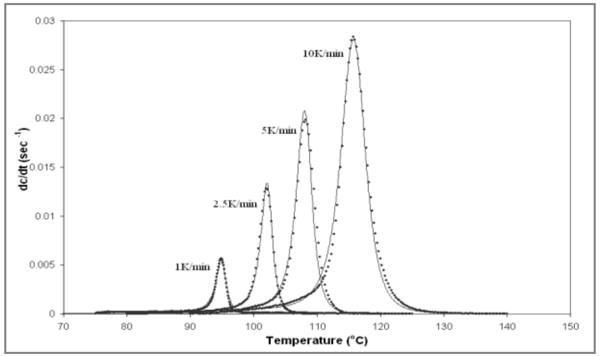


$$x_i = \alpha_{i0} + \alpha_{i1}T + \alpha_{i2}T^2 + O\left(T^3\right)$$

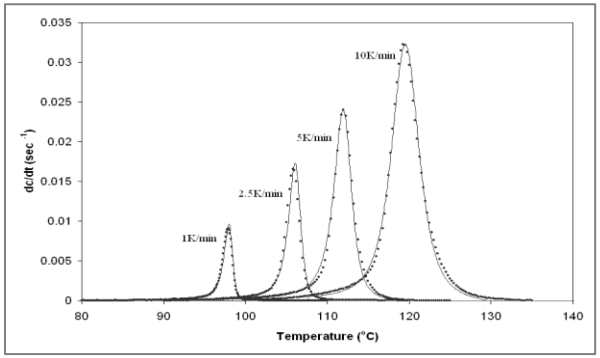
$$\begin{Bmatrix} m \\ n \\ a_1 \\ a_2 \\ E_2 \end{Bmatrix} = \begin{bmatrix} \alpha_{11} & \alpha_{12} & \alpha_{13} \\ \alpha_{21} & \alpha_{22} & \alpha_{23} \\ \alpha_{31} & \alpha_{32} & \alpha_{33} \\ \alpha_{41} & \alpha_{42} & \alpha_{43} \\ \alpha_{51} & 0 & 0 \end{bmatrix} \begin{Bmatrix} 1 & T & T^2 \end{Bmatrix} + O\left(T^3\right) = [\mathrm{a}]\begin{Bmatrix} 1 & T & T^2 \end{Bmatrix}$$

Liquid Silicone Rubber

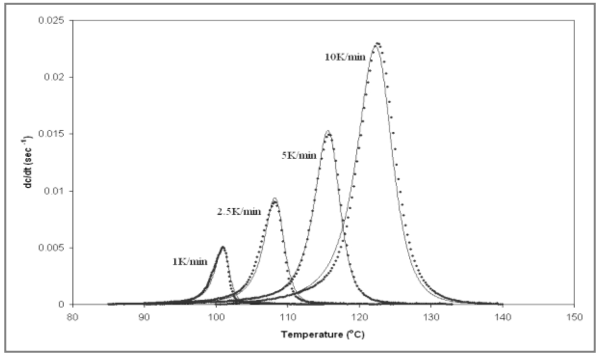
3088/20



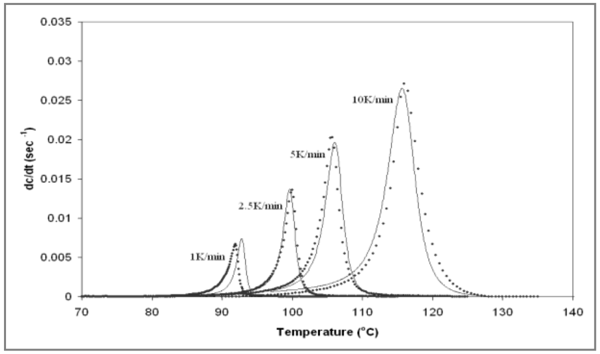
3088/30



2050

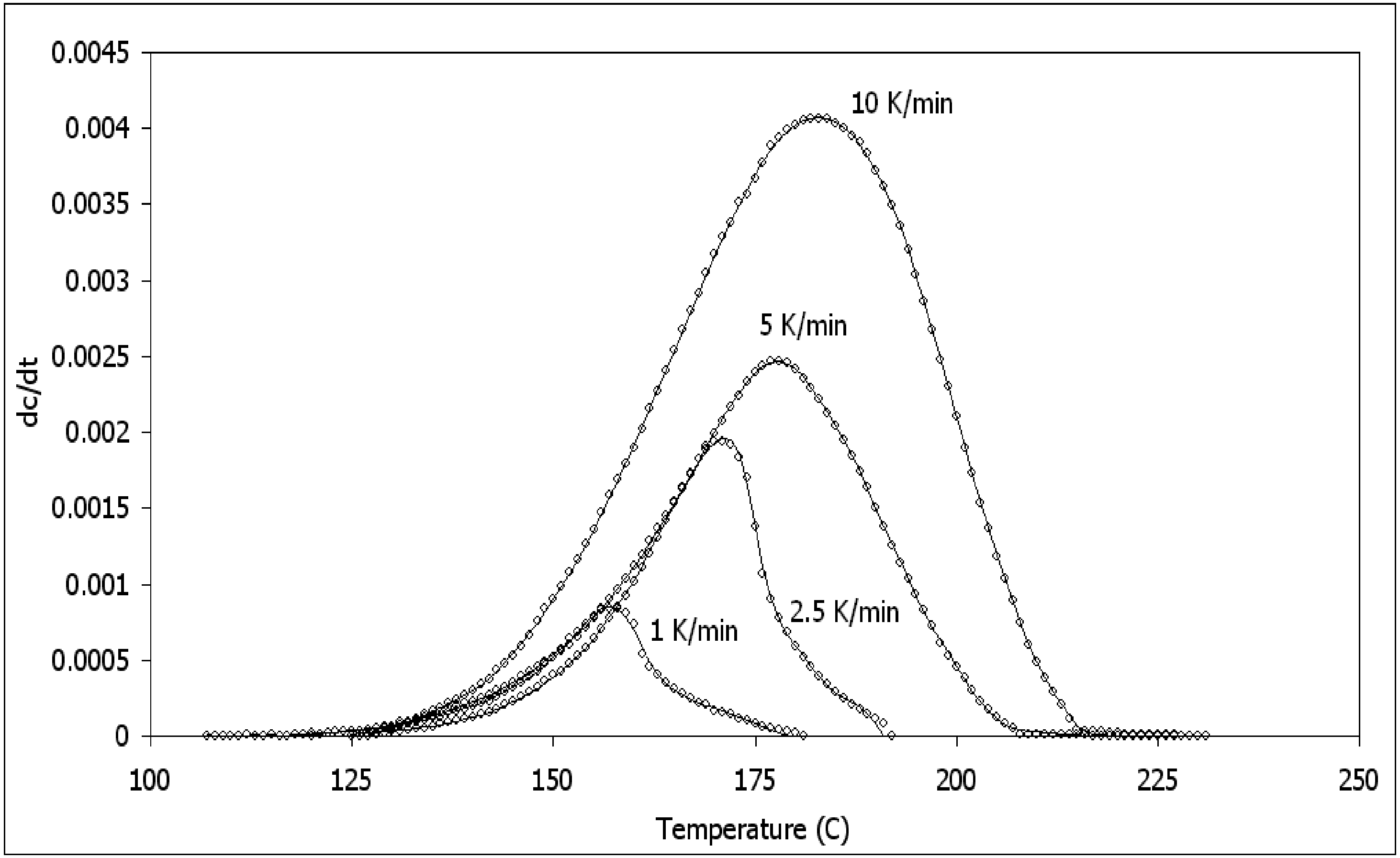


2060



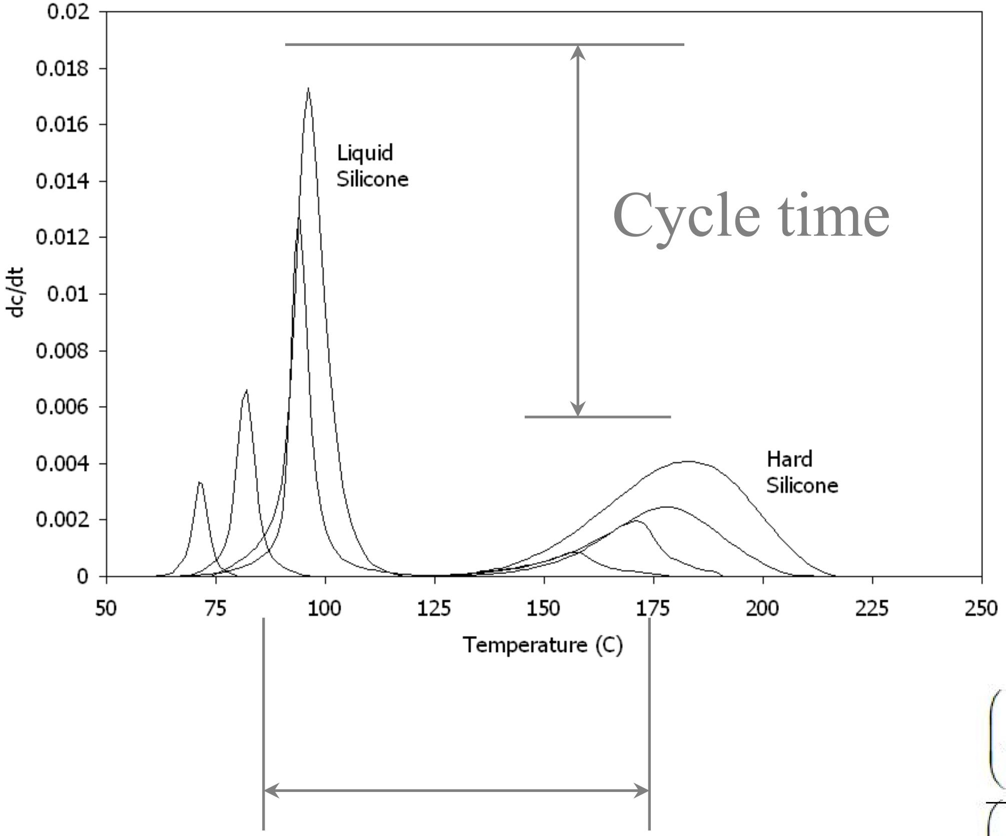
AN ISO 9001 & 13485 CERTIFIED COMPANY

Hard Silicone Rubber



simtec® SILICONE PARTS
AN ISO 9001 & 13485 CERTIFIED COMPANY

Silicone Comparison



Cycle time

Energy cost, cycle time

$$\frac{\left(\frac{dc}{dt}\right)_{\max,LSR}}{\left(\frac{dc}{dt}\right)_{\max,HSR}} = \frac{0.018}{0.004} = 4.5$$

$$\frac{\left(\frac{J}{kg}\right)_{100C,LSR}}{\left(\frac{J}{kg}\right)_{180C,HSR}} = \frac{80}{160} = 0.5$$

AN ISO 9001 & 13485 CERTIFIED COMPANY

Process Optimization

- Material characterization
- Modeling the material kinetic
- Process simulation

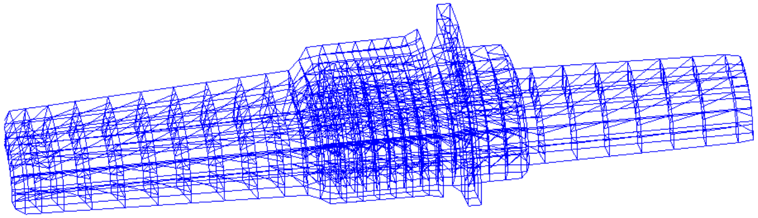
Kamal-Sourour Model

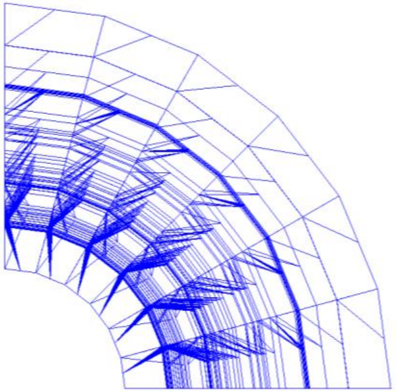
$$\frac{dc}{dt} = \left(k_1 + k_2 c^m\right)\left(1 - c\right)^n = \frac{\dot{Q}}{Q_T}$$

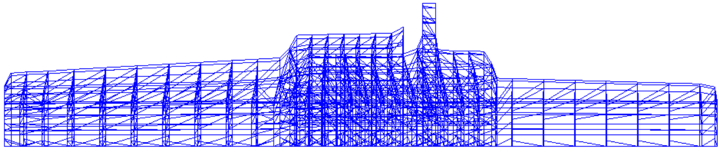
Energy Balance Equation

$$\frac{\partial}{\partial t}\left(\rho C_p T\right) = \frac{\partial}{\partial x_j}\left(k \frac{\partial T}{\partial x_j}\right) + \rho \dot{Q}$$

3D Simulation





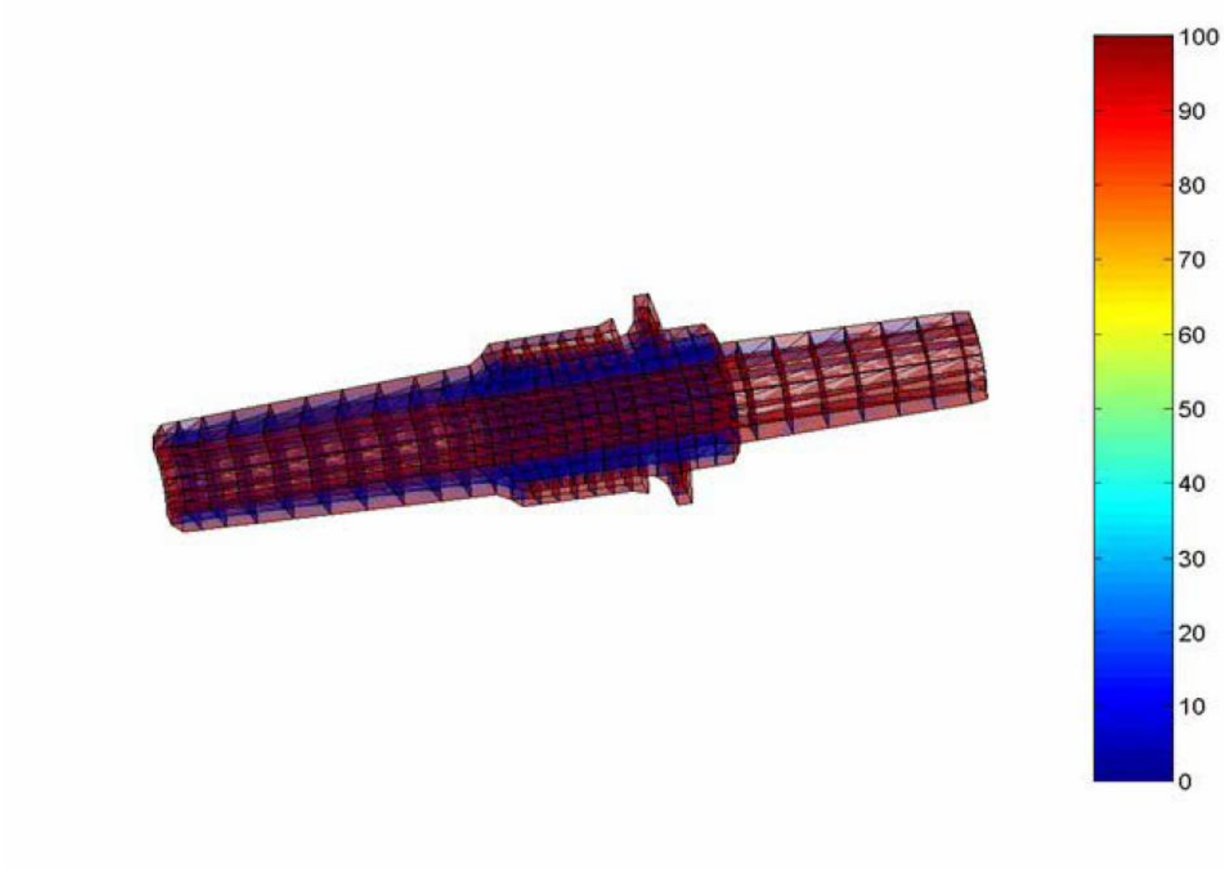


20 noded quadratic elements

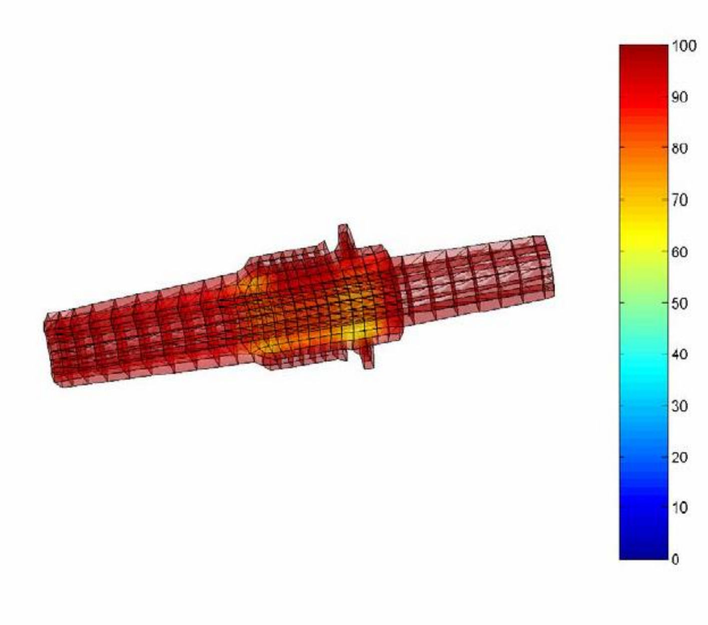
Number of elements = 486

Number of node points = 3100

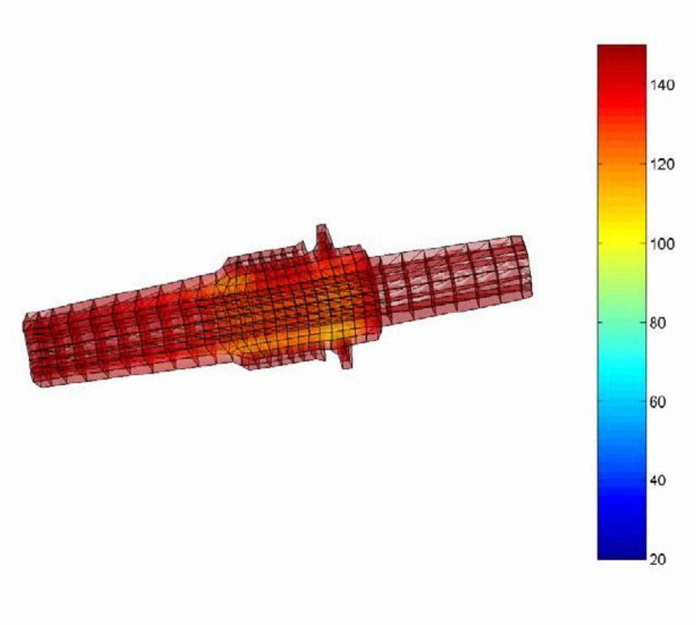
LSR, Mold at 150ºC 1 min



LSR, Mold at 150ºC 1 min



Cure after 1 min

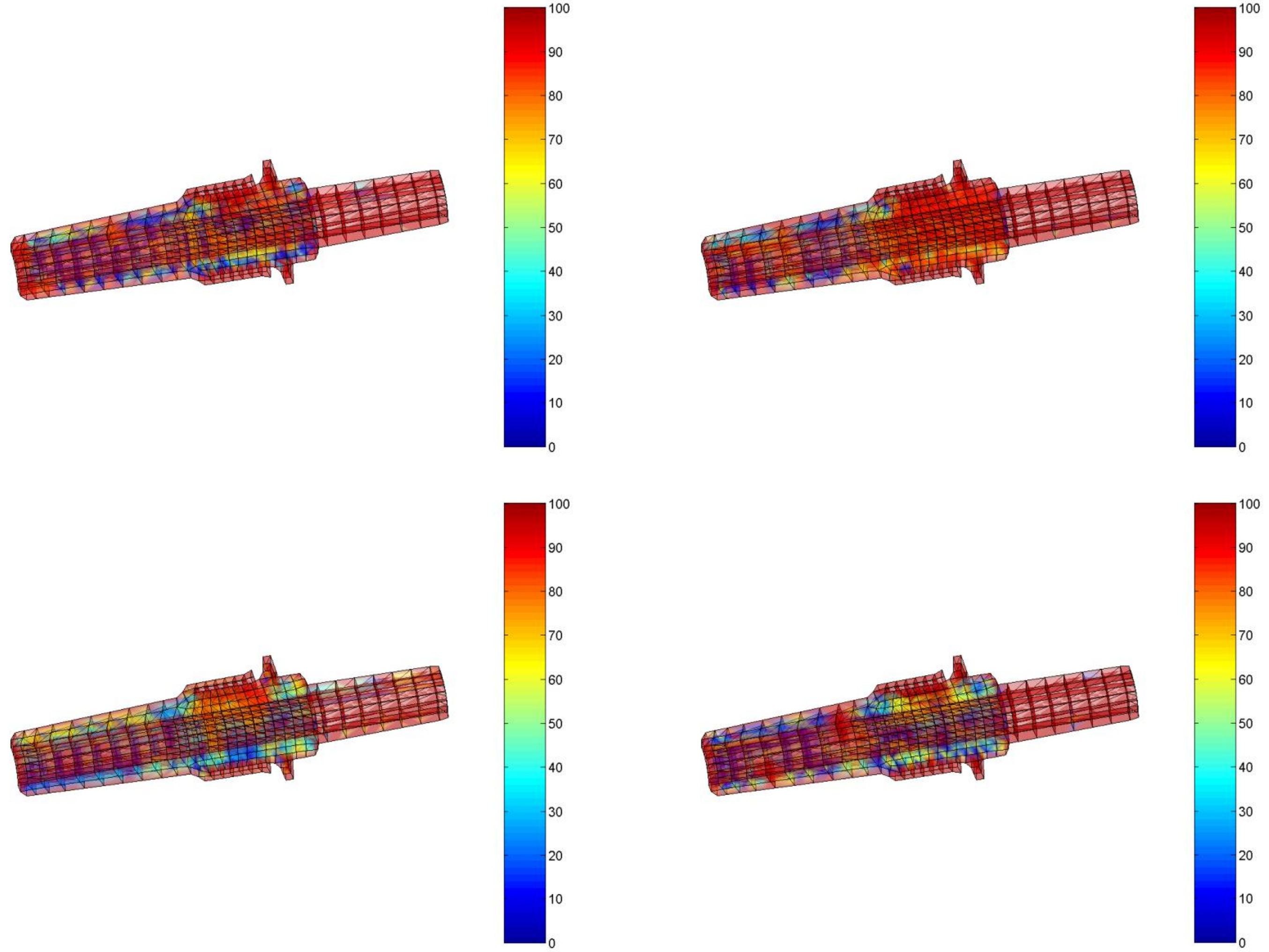


Temperature after 1 min

SILICONE PARTS

AN ISO 9001 & 13485 CERTIFIED COMPANY

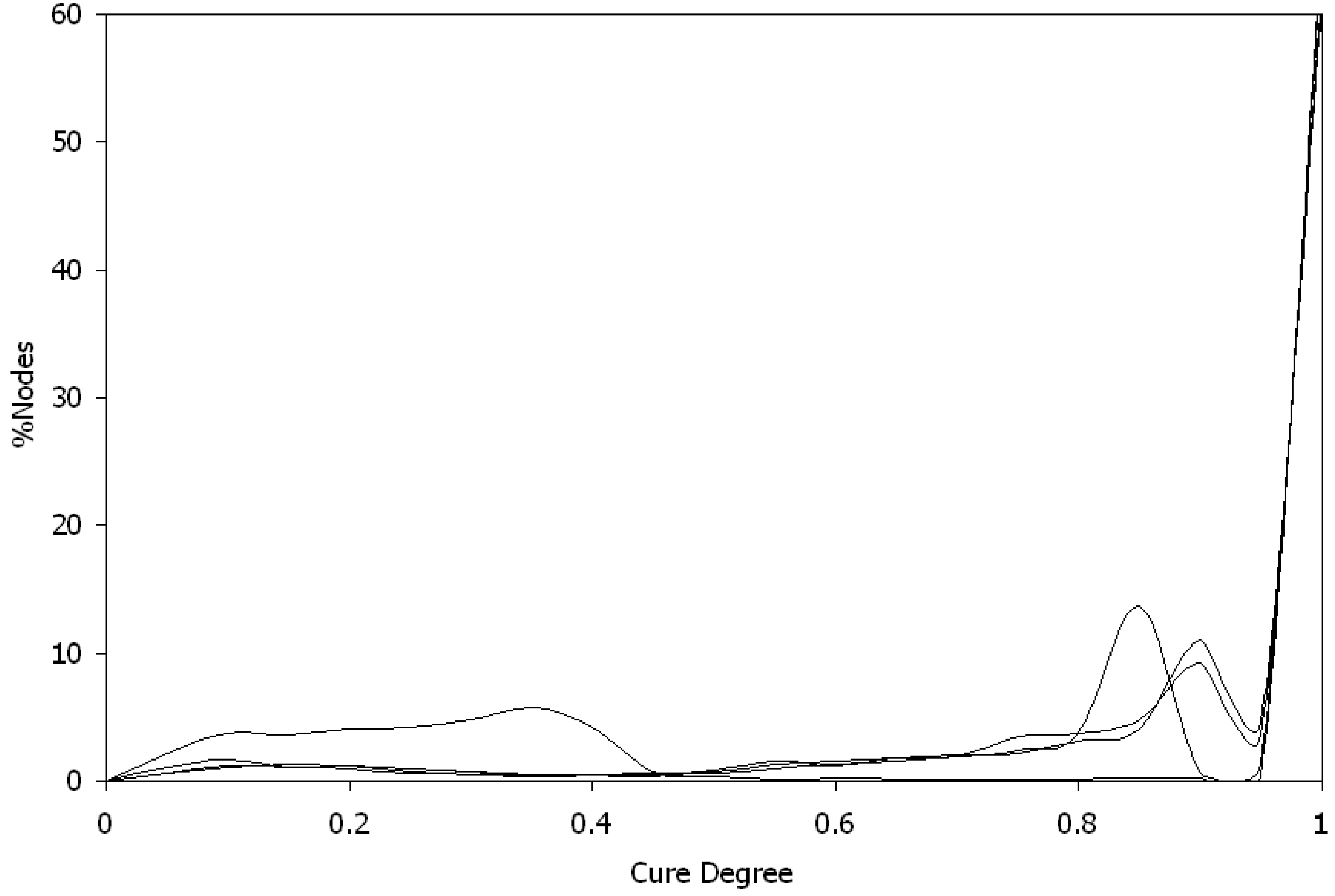
Cure Degree: HCR, Mold at 250ÜC 3 min



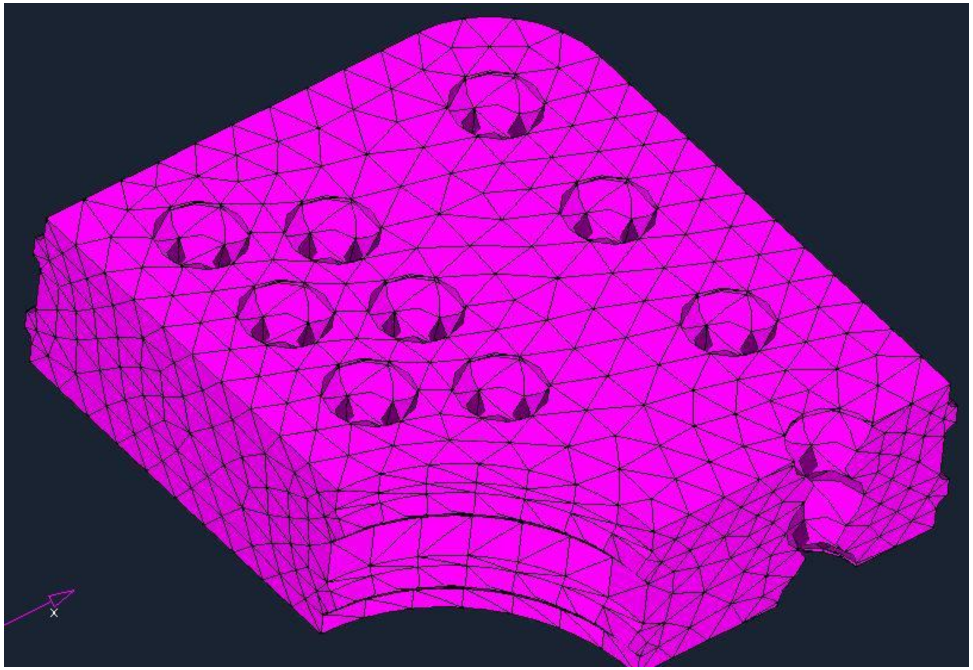
AN ISO 9001 & 13485 CERTIFIED COMPANY

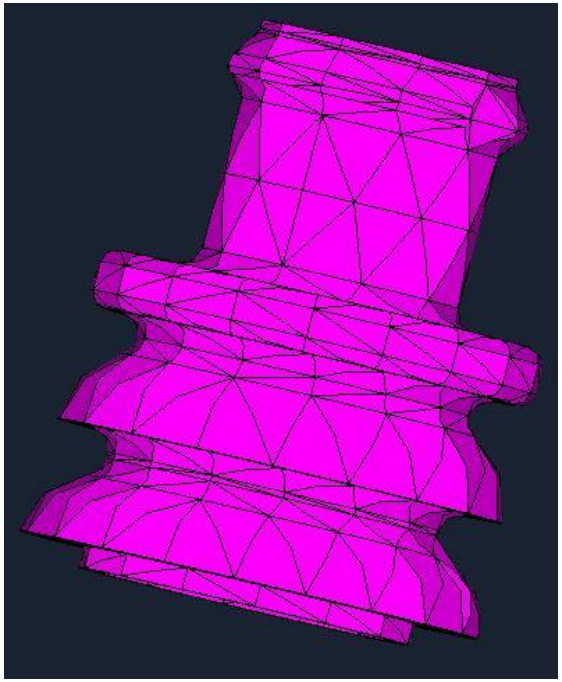
Where Science Meets Innovation™

Cure Degree: HSR, Mold at 250ÜC 3 min

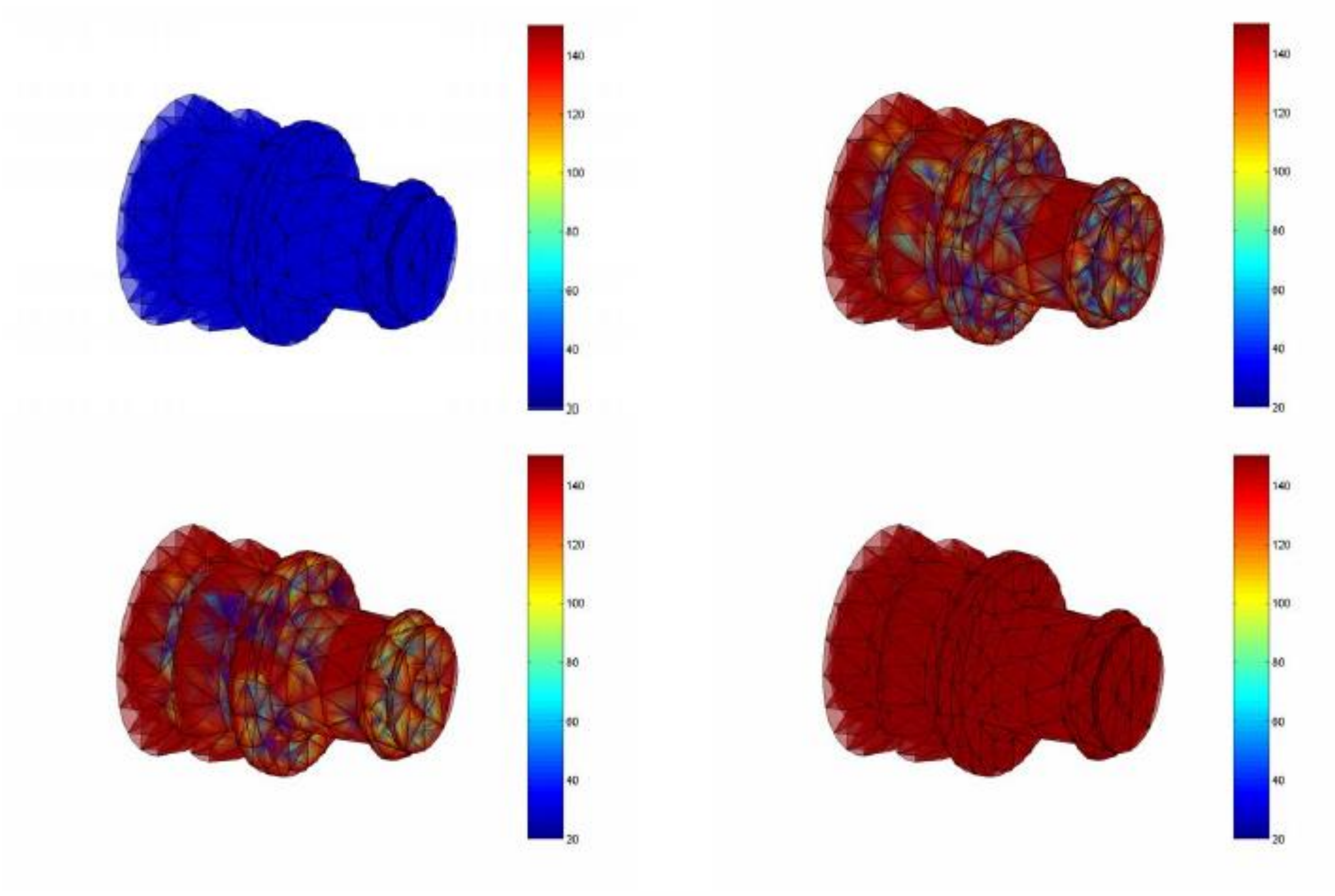


3D Simulation Improvements

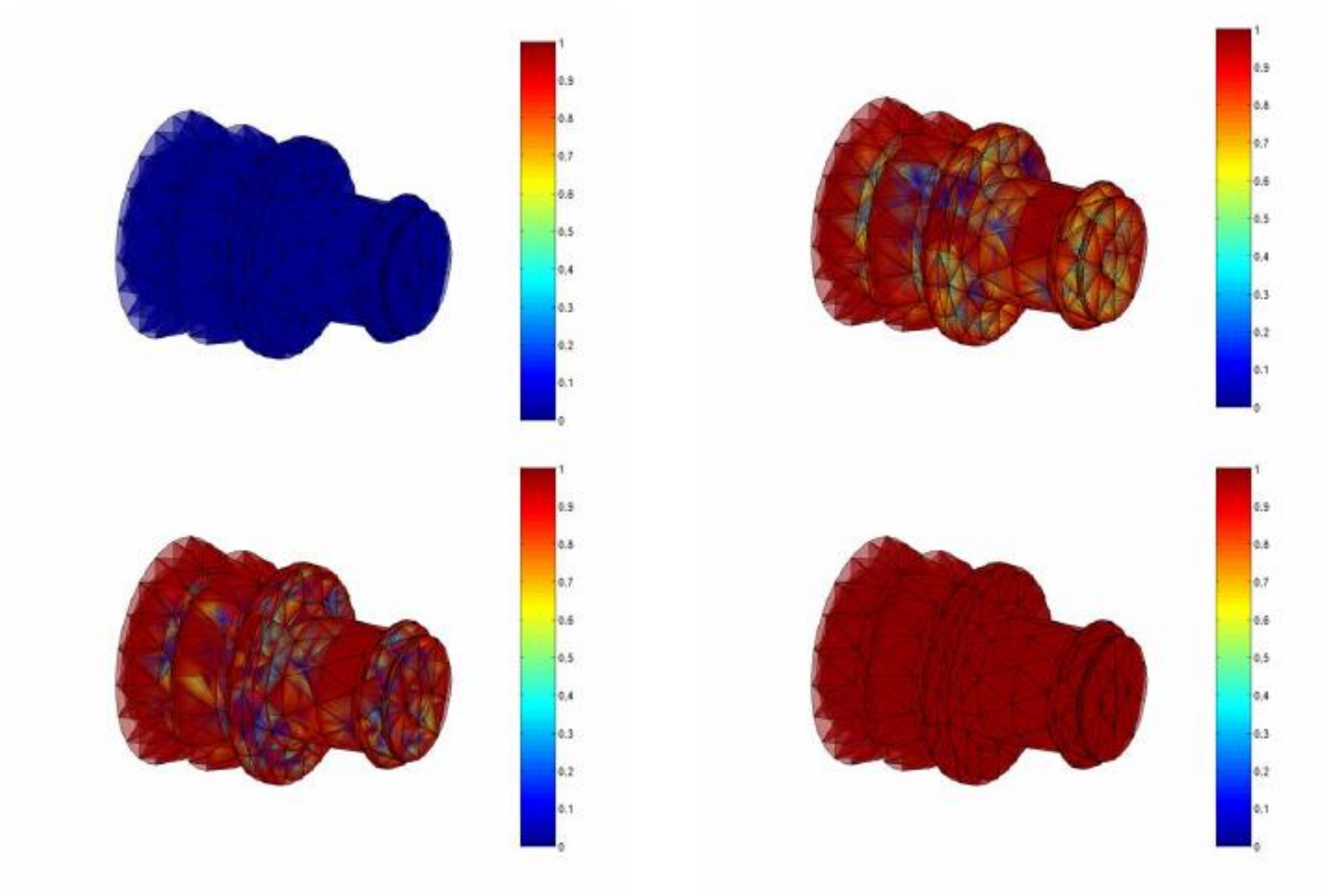




Preliminary Results (Temperature)



Preliminary Results (Curing)



Conclusions

- The kinetics of hard and liquid silicone rubber were characterized using DSC data
- Kamal-Sourour and Kissinger equations were used to model the kinetics
- Processing LSR presents advantages in energy consumption and cycle times
- Aging is the most important inconvenient for the HSR

SILICONE PARTS

AN ISO 9001 & 13485 CERTIFIED COMPANY

Chapter 6

A Study of Injection Molded LSR for Syringe Applications

A Study of Injection Molded Liquid Silicone Rubber for Syringe Applications

Enrique Camacho* and Tim Osswald**

*SIMTEC Silicone Parts LLC, Miramar, FL USA

**Polymer Engineering Center, University of Wisconsin-Madison, USA

INTRODUCTION

Over the past 50 years, silicone rubbers have become increasingly popular. This thermoset elastomer maintains its chemical, mechanical and electrical properties over a wide range of temperatures, and is therefore a natural choice for applications where high precision, stability, consistency and purity is required such as in medical devices and applications to automotive and aerospace components (1,2). It is used for the production of seals in the automotive and aerospace industry, connectors and cables for appliances and telecommunications, implants and devices for medical purpose, and packaging and baking pans for the food industry. Because of its purity, liquid silicone rubber (LSR) has gained a particularly important place as a material for medical applications.

Liquid silicone rubber is a prime candidate as a replacement for other elastomers such as polyisoprene. One application where it has not entered is in the manufacture of rubber syringe tips or stoppers. One of the most significant issues in syringe performance is the consistency of the material, and consequently the magnitude and consistency of the friction between the stopper and the polypropylene barrel of the syringe. Critical here for the end-user of a syringe, is the breakout force and the sustainable force during operation.

A study of the material behavior of liquid silicone rubber for injection molding syringe applications was performed at SIMTEC Silicone Parts, LLC, the University of Wisconsin-Madison and the University of Erlangen-Nuremberg. The experimental and theoretical research demonstrated that liquid silicone rubber has many advantages over its high cure rubber (HCR) and polyisoprene counterparts. LSR proved to be more consistent then HCR and required shorter curing times at lower processing temperatures, which is more likely to assure full cure at the end of a molding process. In this study the friction properties of LSR was measured and compared to the friction properties of polyisoprene rubber. LSR proved superior in all levels to its isoprene counterpart. This opens the opportunity for the manufacture of syringe stoppers made from LSR that will result in reduced break-out effects and lower sustainable forces. In this paper, for the first time, the friction and curing studies performed in this study are published.

BACKGROUND

Silicone rubber is a family of thermoset elastomers that have a backbone of alternating silicone and oxygen atoms and methyl or vinyl side groups. The solidification process of all heat-activated cure thermosets, including silicone rubber, is dominated by an exothermic and irreversible chemical reaction called vulcanization, or cure. The vulcanization process forms a three dimensional network which improves the properties of the final product (2-5). Two types of reactions can lead to vulcanized silicone rubber, peroxide and platinum catalyzed crosslinking (6). Silicone rubbers consist mainly of silicone polymers and fillers. Silicone rubbers come in two different physical states: liquid and solid. Because they exhibit a high viscosity solid silicone rubbers, commonly referred to as high consistency silicone rubbers (HCR) are processed in the same way as normal organic rubbers. Solid silicone rubbers are formed using linear polymers with molecular weights between 400,000 – 600,000 g/mol. These polymers contain an average of 6,000 siloxy units and are water clear Newtonian liquids with viscosities between 15,000 – 30,000 Pa-s. Solid silicone rubbers are usually vulcanized using a two kinds of peroxide catalyst: aroyl-peroxides and alkyl-peroxides (6). Peroxide catalysts allow for high reaction rates. HCR are preprocessed materials that are vulcanized up to a certain degree and then stored in the form of foil-wrapped bars and packed cartons. To process solid rubbers a sheet is then cut or stamped to the required size and placed into a compression or transfer molder. After vulcanization, the part is removed from the mold, deflashed and freed of the peroxide decomposition products in a post-curing process. Peroxides have been used for several decades, and are still widely used today. However, it is not certain what physiological effects the byproducts that result from such cross-linking processes can have on the human body.

Liquid silicone rubbers (LSR) have the same structure as solid silicone rubbers. However, the chain length of the polydimethylsiloxane used for LSR is lower by a factor of about 6. Therefore, the viscosity of the polymer is reduced by a factor of about 1,000 (1-2). The vulcanization of liquid silicone rubber is almost exclusively carried out with a platinum-catalyzed hydrosilylation reaction that does not generate by-products, particularly important for medical applications. In addition to eliminating toxic residues, other advantages of LSR are more consistent mechanical, electrical and chemical resistance properties. These attributes are added to the fact that the material is not inhibited by oxygen.

Liquid silicone rubbers are supplied in barrels or pales. Because of their low viscosity, these rubbers can easily be injection molded. During the process they are pumped through pipelines and hoses to the vulcanization equipment. The two components (A and B component), as well as pigments, if required for non-transparent applications, are pumped to a static mixer by a metering machine were the vulcanization process may start taking place; during injection molding of liquid silicone rubber, loss of material in the feed lines is avoided using cold runners (6).

CURE KINETICS EXPERIMENTS

Most curing polymers are two-component systems. In the case of liquid silicone rubbers, component A contains a platinum catalyst and component B contains methylhydrogensiloxane for cross-linking, as well as an alcohol inhibitor (8,9). For our experimental measurements the A and B components of the liquid silicone rubbers were stored in a two component cartridge. Cartridges were placed at room temperature with room humidity of 35% in a dark cabinet for storage. The two components were mixed in a 1:1 ratio using a static mixer with 13 mixing elements. Five types of LSR, between Shore 20 and 60, and one type of HCR were analyzed via thermal analysis to determine the progression of the vulcanization processes. The specific properties being studied were peak temperature, heat of reaction, and extent of reaction. Differential scanning calorimeter (10) equipment manufactured by Netzsch (Phox DSC 200 PC) was used to measure the heat of reaction for the samples. Sealed aluminum pans were used to analyze all reactions. The mass of the samples ranged from 10 mg to 30 mg. A sealed empty pan was used as a reference. The total heat of reaction was measured by a dynamic scan from 20°C to 150°C using heating rates of 1.0, 2.5, 5.0, and 10.0 K/min.

Multiple scanning rates were used to gain insight into the effect of time and temperature on the vulcanization reaction. Repeatability of vulcanization was obtained for each liquid silicone rubber and heating rate, however, not for the HSR material. Solid silicone rubbers present lower repeatability than liquid silicone rubber, because the material is pre-vulcanized up to a certain degree before storing. During storage, the rubber continues to cross-link at different proportions, leading to a slab with variable degree of conversion. This inconsistency in the HSR material makes it very difficult to take small samples of equal amount of initial cure for testing as well as processing. During processing this leads to parts that reach final cure at different times, introducing an uncertainty when predicting the process time using predictive kinetic models such as the Kamal-Sourour model.

The data of heating rate and the temperature at which the maximum rate of reaction occurs was plotted, and fitted to a linear model. The activation energy of each silicone rubber was calculated with the data from the four dynamic scanning rates tested. The slope of the line corresponds to the negative ratio of the activation energy and the universal gas constant as can be seen for the LSR Shore 50 in Figure 1.

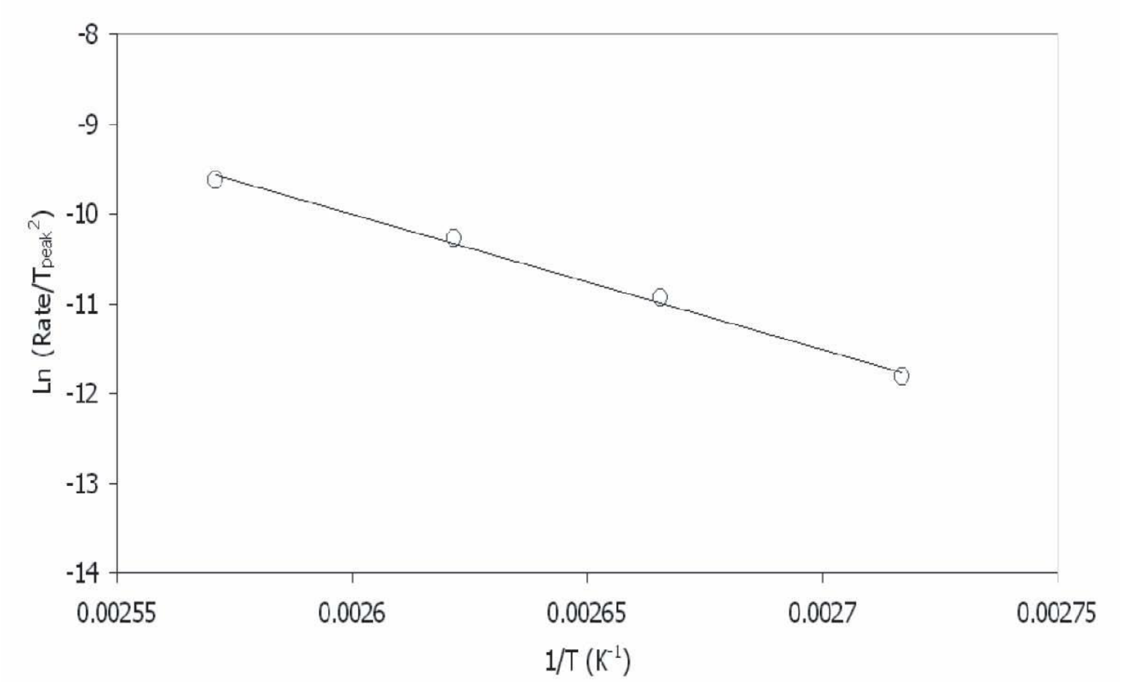


Figure 1. Kissinger model for an LSR Shore 50.

The data obtained from the dynamic DSC scans was used to determine the kinetic constants for the Kamal-Sourour kinetic model. This process was done by fitting the instantaneous vulcanization rate and the percentage of vulcanization at each specific temperature into a model that describes the reaction. The technique uses one or more dynamic DSC scans to determine a set of kinetic parameters that model the vulcanization process for all the heating rates tested. The experimental data and fitted Kamal-Sourour model for the Shore 50 liquid silicone rubber are graphed Figure 2. The fitted models are in good agreement with the DSC data.

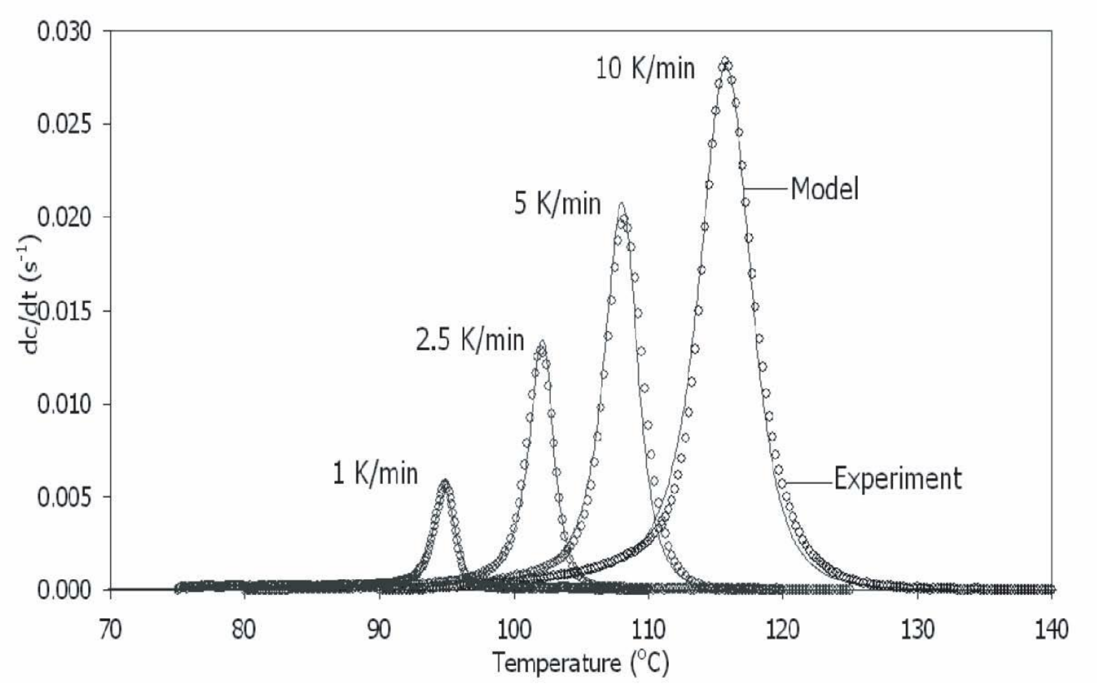


Figure 2. Fitted model and experimental data for an LSR Shore 50.

The results of HCR and one type of LSR were also compared. Various material samples were taken from one HCR batch and tested (9). Due to the variation in the initial degree of cure between the samples, only one was chosen to fit the model. Figure 3 presents the fitted data and compares it to a HCR for similar applications. As can be seen HCR vulcanizes at higher temperatures than LSR leading to larger cycle times and energy costs. In addition, the vulcanization rate of LSR is higher than the one of HCR. A higher reaction rate will significantly reduce the cycle time.

FRICTION EXPERIMENTS

The kinetic friction coefficient of friction was measured between two types of liquid silicone rubber of 50 and 70 shore hardness, as well as a polyisoprene for comparison, and an unnucleated polypropylene . To measure the kinetic friction coefficient between the elastomers and the polypropylene, small 6mm diameter discs where cut from the 3 mm thick elastomer sheets and bonded into a 1mm deep indentation of the fixture. The rubber elements were pressed against a rotating 110 mm diameter polypropylene disc molded of an un-nucleated material from Basell. The experiments were performed at the Plastics Technology Institute at the University of Erlangen-Nuremberg. This was the first time that a cured material, and elastomer, were tested against a thermoplastic material. As a consequence, the tests had to be adjusted due to the large difference between elastomers and thermoplastics, such as the significantly larger compliance of elastomers. Table 1 summarizes the experimental set-up and parameters. It should be noted that while the standard testing pressure is 1 N/mm2, a lower pressure of 0.5 N/mm2 had to be used for the polyisoprene sample. This was due to the fact that at the standard pressure the polyisoprene sample experienced an oscillatory stick-slip condition that made it impossible to record an accurate friction force, and consequently coefficient of friction.

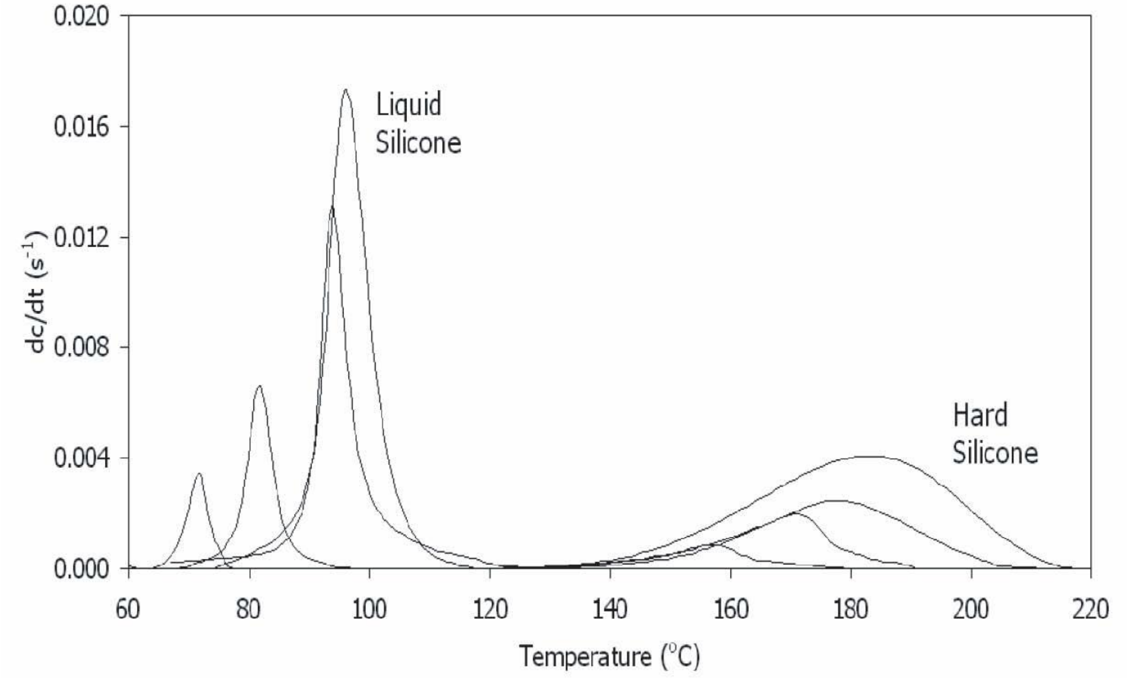


Figure 3. Comparison of curing reactions for comparable LSR and HCR materials

Table 1. Friction Test Parameters

Parameter	Specification
Testing Temperature	23°C
Lubricating medium	none (dry)
Rubber sample size	6 mm diameter
Polypropylene disc size	110 mm diameter
Speed	0.05 m/s
Pressure (LSR)	1 N/mm^2
Pressure (Polyisoprene)	0.5 N/mm^2

Table 2 presents the friction measurements results. As can be seen, the Shore 50 LSR presented the lowest coefficient of friction; almost half the coefficient of friction between polyisoprene and polypropylene. All three tests were very repeatable, with relatively low standard deviations.

Table 2. Friction Test Results Between Rubber Samples and Polypropylene Disc

Material	Coefficient of Friction	Standard Deviation
LSR Shore 50	0.67	0.05
LSR Shore 70	1.01	0.06
Polyisoprene	1.23	0.03

CONCLUSIONS

The main conclusion from this study is that LSR is a consistent material that renders a reproducible process and product. The accurate metering and mixing that occurs during processing of LSR renders a product with consistent properties. This study demonstrated how the curing behavior of LSR occurs at significantly lower temperatures than HCR, leading to lower energy consumption during processing. Furthermore, the reaction rates with LSR are much lower than with HCR, resulting in lower cycle times, furthermore adding to energy and production costs. Most importantly for medical applications, specifically syringes, our studies show that the friction coefficient between LSR and polypropylene are significantly lower than the friction between polyisoprene (currently being used to manufacture syringe stoppers) and polypropylene. These finding open doors to a new application for LSR that will most probably render products of higher quality with reproducible functionality. An additional benefit of employing LSR for syringe stoppers is the high purity of the material, which certainly broadens the application of such stoppers for syringes. Compatibility issues need, however, to be studied by the syringe manufacturers and suppliers.

ACKNOWLEDGMENTS

The authors would also like to thank Julian Salguero of the Polymer Engineering Center at the University of Wisconsin-Madison for assisting in the cure kinetic experimental work, and Robert Feulner of the Plastics Technology Institute at the University of Erlangen-Nuremberg for performing the friction experiments.

REFERENCES

1. G. Koerner, M. Schulze, J. Weis, *Silicones, Chemistry and Technology*, CRC Press, Boca Raton (1991).
2. W. Noll, *Chemistry and Technology of Silicones*, Academic Press, New York (1968).
3. T.A. Osswald and G. Menges, G., *Material Science of Polymers for Engineers*, 2nd Edition, Hanser-Gardner Publications, Cincinnati (1996).
4. R.J. Young and P.A. Lowell, *Introduction to Polymers*, 2nd Edition, Stanley Thornes Publishers Ltd, Great Britain (2000).
5. Odian G, *Principles of Polymerization*, 3rd Edition, John Wiley & Sons, New York (1991).
6. L. Lopez, *Modeling the Vulcanization of Liquid Silicone Rubbers*, M.Sc. Thesis, Department of Mechanical Engineering, University of Wisconsin-Madison, Madison (2004).
7. Cosgrove, L. Lopez, J.P. Hernandez-Ortiz, T.A. Osswald and E. Camacho, *SPE ANTEC 2004*, Chicago (2004).
8. D. Cambell, R.A. Pethrick and J.R. White, *Polymer Characterization: Physical Techniques*, 2nd Edition, Stanley Thornes Publishers Ltd, Great Britain (2000).

Chapter 7

Assembly Injection Molding

Assembly Injection Molding

Alejandro Roldán-Alzate [1], Enrique Camacho [2], Tim Osswald[1]
1. Department of Mechanical Engineering, University of Wisconsin-Madison, Madison, WI
2. SIMTEC Silicone Parts, Miramar, FL

Introduction

With SIMTEC's Liquid Silicone Rubber (LSR) processing know-how and technology, it is now possible to integrate — into one assembly — functions of parts with complex design, challenging geometry, and tight tolerances. Assemblies are injection molded, employing the same material or a combination of materials to enhance their functioning. Assembly injection molding is primarily completed by either *2-Shot injection* or *over-molding* processes. These are highly sophisticated molding processes that provide increased design flexibility for making multi-material, multi-color, and multi-functional components at a competitive cost. We paused bakeware as it was triggering a lot of expensive and irrelevant searches for individual products This process is ideal for function and part integration into one single component. By employing the right technology, experience, and knowledge, assembly injection molding comparatively offers several benefits over traditional processing techniques.

These benefits include the elimination of:
- Unnecessary assembly steps
- Quality checks for several parts
- The need for independent tools for each material
- The multiple validation costs needed for each independent tool

Additional benefits include:
- Increased and more sustainable quality levels
- Optimized part design
- Reduced material consumption
- Reduction of capital investment due to part and function integration
- Reduction of procurement costs by dealing with one source

There are many applications where assembly injection molding of LSR and thermoplastics and/or metals plays a significant role in the industry. These include:

- *Sanitary articles* - showerheads and diffusers.
- *Personal care articles* - mascara applicators, electric shaving machines, and toothbrushes
- *Health care articles* - valves, flow meters
- *Electronic and communication devices* - soft-touch interfaces
- *Food contact applications* - infant feeding items, juice dispensers, coffee makers, and dairy product dispensers and filling machines
- *Automotive applications* - connectors, soft-touch components, navigation system aids

Process

Assembly injection molding requires the use of a two-shot LSR/substrate processing line. This technology enables us to achieve the best performance out of materials with complementary chemical and physical properties. By employing this technology, the necessity of post molding assembly lines and/or secondary operations, such as surface treatments, are reduced or even eliminated. Either a rotating mold or transfer tools are needed to enable the production of ready components in one cycle. Both kinds of tools are in operation at SIMTEC.

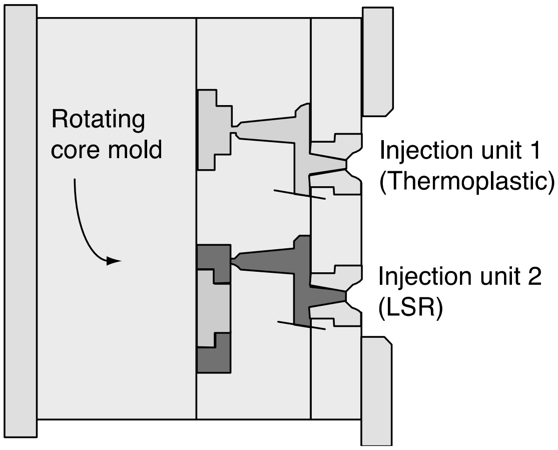


Figure 1: Schematic diagram of a rotating mold used to produce multi-component injection molded parts.

Assembly injection molding is a special process used in the plastic processing industry encompassing over-molding, multi-component injection molding, two-shot injection molding, multi-shot injection molding. It is sometimes referred to as an *in-mold assembly* process. However, this process is different from *co-injection molding* which also incorporates two different materials into a single molded part. Co-injection molding involves the sequential and/or concurrent injection of two dissimilar but compatible materials into a cavity to produce parts that have a sandwich structure with the core material embedded between the layers of the skin material. In assembly injection molding, on the other hand a thermoplast is first molded and then transferred to a different cavity to be molded with LSR inside a cavity defined by the surfaces of the insert and the tool. The adhesion between the two different materials can be mechanical and/or chemical, as needed.

Conventional assembly injection molding dates back several decades. This process has since advanced to allow consistent, cost-effective production of multicolor or multifunctional products in a variety of both innovative and commonly used methods. The choice of a suitable molding technique depends on the production volume, quality requirements, and the molder's experience and know-how. For example, one can use two separate molds and a stand-alone, single-material, conventional injection-molding machine for producing the assembly for injection molded parts via over-molding. In this approach, the insert is first molded and then transferred to a second mold, where it is overmolded with a second polymer or elastomer. The disadvantage of this approach is that it involves additional steps to transfer and load the prefabricated insert into the second mold. However, if the part weight and cycle time are radically different for each material, then this is a viable and economically advisable way of manufacturing the assemblies.

Another method employed for assembly injection molding calls for a rotating mold and multiple injection units, as shown in Fig. 1. Once the insert is molded, a hydraulic or electric servo drive rotates the core and the part by 180 degrees (or 120 degrees for a three-shot part), allowing alternating polymers to be injected. This is the fastest and most advisable method, because two or more parts can be molded every cycle. Utilities for the rotating mold (i.e., cooling water, compressed air, or special heating) are connected through a central rotary union. If there is a family of parts that requires rotational transfers, it is more economical to have the frictional capability built into the machine (and pay for it once) than it is to buy a family of molds each requiring the capability.

Another variation of multi-component injection molding involves automatically expanding the original cavity geometry using retractable (movable) cores or slides while the insert is still in the mold. This process is called a *core-pull* or *core-back* technique, and is shown in Fig. 2. In this case, the core retracts after the insert has solidified to create open volume to be filled by the second material within the same mold.

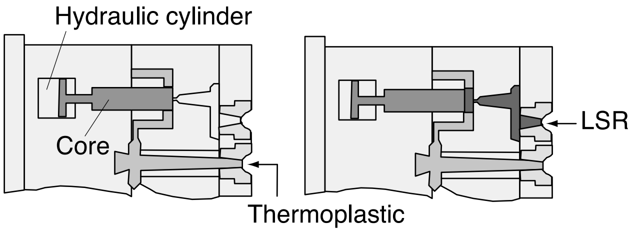


Figure 2: Schematic diagram of multi-component injection molding using a *core pull* or a *core back* technique.

Material selection is vital for multi-component injection molding. A thorough analysis needs to be conducted to determine material compatibility, chemical and wear-resistance, environmental performance, and other program-specific requirements. One of the benefits of employing LSR is that flexible transparent – or if need be, high-transparent – thermoplastics can be molded onto a rigid substrate to create a soft-touch feel, thereby improving the handling in a finished assembly. SIMTEC has experience with the two-shot injection molding of several thermoplastic materials and LSR. Our Technical Bulletin Vol. 1, Issue 2 further elaborates on the state-of-the-art technology for two-shot injection molding.